NEW YORK UNIVERSITY
COURANT INSTITUTE-LIBRARY

NYO-1480-151

Courant Institute of
Mathematical Sciences

AEC Computing and Applied Mathematics Center

Exact Solution of the First-Order Perturbed Percus-Yevick Equation for Arbitrary Pair Potentials

Jerome K. Percus and Sheldon Shanack

AEC Research and Development Report

Physics
June 1970

NYO-1480-151

New York University

NEW YORK UNIVERSITY
COURANT INSTITUTE-LIBRARY

UNCLASSIFIED

AEC Computing and Applied Mathematics Center
Courant Institute of Mathematical Sciences
New York University

Physics NYO-1480-151

EXACT SOLUTION OF THE FIRST-ORDER PERTURBED PERCUS-YEVICK EQUATION FOR ARBITRARY PAIR POTENTIALS

Jerome K. Percus and Sheldon Shanack

Contract No. AT(30-1)-1480

UNCLASSIFIED

Table of Contents

I. Introduction.. 1

II. Distribution Functions in Classical Equilibrium Statistical Mechanics.................................. 3

- A. Coordinate Distribution Functions in a Grand Canonical Ensemble.......................... 3
- B. The Pair Correlation Function....................... 7

III. Integral Equations for the Pair Correlation Function..10

- A. Functional Taylor Expansion........................10
- B. The Generating Functional..........................12
- C. Bootstrap Operation................................17
- D. Integral Equations.................................23
  - 1. The Direct Correlation Function................23
  - 2. The Percus-Yevick Equation.....................25

IV. The First-Order Perturbed P.Y. Equation..............28

V. Solution of First-Order Perturbed P.Y. Equation: One Dimension...32

- A. Conversion to a Differential Equation..............32
  - 1. Sth-Neighbor Structure of $\gamma(x)$ and $\Gamma(x)$.........32
  - 2. Evaluation of $\Gamma''(x)$.............................38
  - 3. Correlation Function Inside the Hard Cores......40
- B. Solution of Differential Equation..................41
  - 1. Reduction of Inhomogeneous Term..................41
  - 2. Linear Dependence of Integration Constants......43
  - 3. Continuity Conditions at Hard-Core Boundary.....45
  - 4. Explicit Equations for the Two Arbitrary Constants......................................48

VI. Comparison with Exact Results........................51

- A. Extended Hard Core Kernel..........................51
- B. Calculation of $\Delta(x)$..................................53
- C. Calculation of Direct Correlation Function.........58

VII. Applications..63

- A. Hard Cores with Surface Adhesion...................63
- B. The Debye-Huckel Model.............................65
- C. Long-Range Forces..................................68

Appendix A...72

Appendix B...74

Bibliography...76

ABSTRACT

The effect upon the correlation functions of a fluid of adding a pair potential of arbitrary range to a repulsive hard core is investigated in the case of the Percus-Yevick approximation of classical equilibrium statistical mechanics. The nonlinear P.Y. equation is perturbed, to first-order, and the resulting linear integral equation for the first-order correlation functions is then solved exactly for a general interparticle potential. The method of solution is presented for one-dimensional systems, but three-dimensional non-polar and polar liquids can be encompassed. Essential to the technique is the calculation of a certain zeroth-order quantity, which is proportional to the Faltung of the hard core pair correlation function with itself, and which is composed of a sum of n*th*-neighbor contributions. Obtaining this quantity allows conversion of the first-order perturbed P.Y. integral equation to an ordinary differential equation of fourth order for the direct correlation function inside the core. Reduction of the inhomogeneous term and determination of the constants of integration by application of the continuity conditions at the hard core boundary results in explicit expressions for the first-order direct correlation function inside the core, and the first-order pair correlation function outside the core. The validity of the first-order perturbation theory is tested by evaluating the expression obtained for the first-order direct correlation function in the particular case of a tail potential which is a replica of the core over a finite range. A linear dependence results, in agreement with exact statistical mechanics. A simple application is made to the glue model of Baxter. If the phenomenon of linearity is extrapolated as a model for arbitrary tail potential, and the P.Y. equation is further simplified to the Debye-Huckel model with hard-core insertion, a number of explicit solutions may be obtained. This is carried out for Yukawa tail, double Yukawa, and power law tails.

I. Introduction

The Percus-Yevick approximate integral equation for the pair correlation function in classical statistical mechanics has been solved exactly for hard cores [13]. The direct correlation function is given in its non-vanishing domain by a low order polynomial, of degree one or three, for the case of one or three - dimensional hard cores. Exact solutions of the P.Y. equation for potentials of arbitrary range have never been obtained, however. The object of this work is to examine the effect upon the correlation functions of adding a long-range interaction to the repulsive core. Although treated exhaustively in one-dimension, our technique is by no means limited to this, indeed being applicable to both three-dimensional non-polar and polar liquids.

We commence, in Sections II and III, by reviewing the formalism of distribution functions in the equilibrium theory of classical fluids [1,6]. The pair correlation function is defined, and its role in determining the thermodynamics of an N-particle system is discussed. By utilizing a functional Taylor expansion combined with the relation between the density of a nonuniform system and the pair correlation function of a uniform system, approximate integral equations for the pair correlation function can be derived [3]. By this technique, the Percus-Yevick equation is obtained. In Section IV, the pair potential is written as the sum of two parts, a repulsive hard core plus a tail potential of arbitrary range. Making use of the fact that the P.Y. equation has been solved exactly for hard cores, we perturb to obtain the first-order Percus-Yevick equation. This is followed, in Section V, by a detailed description of the method of solution of this first-order perturbed integral equation. Expressions for the first-order direct correlation function and pair correlation function are given. In the following section, the perturbation theory is tested by evaluating the expression obtained from it previously for the correlation function in the case of a hard core tail potential of finite range. Comparison of the first-order correlation function with its counterpart from exact statistical mechanics is made and the results are discussed. The last section contains a number of explicit solutions for potentials consisting of a hard-core plus tail. First order phase transitions are found to occur for each model studied.

II. Distribution Functions in Classical Equilibrium Statistical Mechanics.

We begin by reviewing the formalism of distribution functions in the theory of classical fluids. For the present, we consider a single-component simple fluid whose total internal potential energy is given by the sum of pair interactions. Later, the method of distribution functions will be extended to a more general type of potential energy. The assumption of two-body interparticle forces, viz., that the force between any pair of particles is independent of the presence of any additional particles, has as a consequence that the equation of state depends only on the two-body distribution function and not upon higher order distribution functions.

A. Coordinate Distribution Functions in a Grand Canonical Ensemble.

Inasmuch as it will be necessary to vary the density arbitrarily, use of the grand canonical ensemble is indicated. Thus, if the fraction of the systems of the ensemble having the composition N in the region $d^N\underline{r}\ d^N\underline{p}$ of phase space appropriate to N is denoted by: $P_N^{(G)}(\underline{r},\underline{p})\ d^N\underline{r}\ d^N\underline{p}$, then the fraction of systems in the ensemble with composition N, viz., the probability that the open system does contain exactly N particles, is merely:

$\int P_N^{(G)}(\underline{r},\underline{p})\, d^N\underline{r}\, d^N\underline{p}$. The integration is over all N-canonical coordinates $\underline{r}_1 \ldots \underline{r}_N$ and momenta $\underline{p}_1 \ldots \underline{p}_N$, and is independent of time. Then

$$\sum_{N=0}^{\infty} \int P_N^{(G)}(\underline{r},\underline{p})\, d^N\underline{r}\, d^N\underline{p} = 1 \; . \tag{2.1}$$

The density function $P_N^{(G)}$ can be written as

$$P_N^{(G)}(\underline{r},\underline{p}) = \frac{1}{Z_G}\, e^{-\beta H_N(\underline{r},\underline{p})}\, \lambda^N \; , \tag{2.2}$$

where $\beta = (kT)^{-1}$, and λ is the fugacity, related to the chemical potential, μ, through $\lambda = e^{\beta\mu}$.

H_N is the N-body system Hamiltonian,

$$H_N = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i \neq j = 1}^{N} \phi(\underline{r}_i,\underline{r}_j) + \sum_{i=1}^{N} U(\underline{r}_i) \; , \tag{2.3}$$

in which the terms are, respectively, the kinetic energy, internal potential energy, and external potential energy. The normalizing factor Z_G is the grand partition function, given by:

$$Z_G = \sum_{N=0}^{\infty} \int e^{-\beta H_N(\underline{r},\underline{p})}\, \lambda^N\, d^N\underline{r}\, d^N\underline{p} \tag{2.4}$$

$$= \sum_{N=0}^{\infty} \lambda^N Q_N \; , \tag{2.4a}$$

where Q_N is the canonical ensemble partition function,

$$Q_N = \frac{1}{h^{3N} N!} \int e^{-\beta H_N(\underline{r},\underline{p})}\, d^N\underline{r}\, d^N\underline{p} \; . \tag{2.5}$$

The momentum integrations in (2.5) are trivial. It may be verified that

$$(2.6) \qquad Q_N = \frac{Z_N}{N!\ \Lambda^{3N}} , \qquad \text{with } \Lambda = \frac{h}{\sqrt{2\pi mkT}} .$$

The quantity Z_N, the configuration integral, is then an N-fold coordinate space integral,

$$(2.7) \qquad Z_N = \int \cdots \int e^{-\beta V_N(\underline{r}_1 \cdots \underline{r}_N)}\, d\underline{r}_1 \cdots d\underline{r}_N ,$$

in which V_N is the potential energy portion of (2.3). Introducing the activity, z, defined by

$$(2.8) \qquad z = \frac{\lambda}{\Lambda^3}$$

we may then write (2.4a) as

$$(2.9) \qquad Z_G = \sum_{N=0}^{\infty} \frac{z^N}{N!} Z_N .$$

In this form each N-particle system of the ensemble is weighted by $z^N/N!$

We next define distribution functions expressing the probabilities of observing different configurations of sets of s particles out of the total number N ($N \geq s$). Let $n_N^{(s)}(\underline{r}_1 \cdots \underline{r}_s)\, d\underline{r}_1 \cdots d\underline{r}_s$ be the probability that, if the configuration of the system of N particles is observed, a particle (not necessarily particle 1) will be found in $d\underline{r}_1$ at $\underline{r}_1$, a second in $d\underline{r}_2$ at $\underline{r}_2$, ..., and another in $d\underline{r}_s$ at $\underline{r}_s$. Then, in the canonical ensemble,

$$(2.10)\quad n_N^{(s)}(\underline{r}_1 \ldots \underline{r}_s) = \frac{N!}{(N-s)!} \; \frac{\int \cdots \int e^{-\beta V_N(\underline{r}_1 \ldots \underline{r}_N)} \, d\underline{r}_{s+1} \ldots d\underline{r}_N}{Z_N}$$

with Z_N defined by (2.7).

For a grand ensemble, we denote by $n_s(\underline{r}_1 \ldots \underline{r}_s) d\underline{r}_1 \ldots d\underline{r}_s$ the probability of observing particles in $d\underline{r}_1, \ldots, d\underline{r}_s$ at $\underline{r}_1, \ldots, \underline{r}_s$. $n_s(\underline{r}_1 \ldots \underline{r}_s)$ is averaged over N and is thus independent of N. Specifically,

$$(2.11)\quad n_s(\underline{r}_1 \ldots \underline{r}_s) = \sum_{N=s}^{\infty} n_N^{(s)}(\underline{r}_1 \ldots \underline{r}_s) \int P_N^{(G)}(\underline{r},\underline{p}) d^N\underline{r} \, d^N\underline{p} \; .$$

The function $n_s(\underline{r}_1 \ldots \underline{r}_s)$ is the s-body distribution function in the grand canonical ensemble; it depends also on T and μ, in addition to $\underline{r}_1, \ldots, \underline{r}_s$.

From (2.2), (2.5), (2.6) and (2.8), it follows that:

$$(2.12)\quad \frac{z^N Z_N}{N! Z_G} = \int P_N^{(G)}(\underline{r},\underline{p}) \, d^N\underline{r} \, d^N\underline{p} \; .$$

Hence, using (2.10) and (2.12), (2.11) may be written as:

$$(2.13)\quad n_s(\underline{r}_1 \ldots \underline{r}_s) = Z_G^{-1} \sum_{N=s}^{\infty} \frac{z^N}{N-s!} \int \cdots \int e^{-\beta V_N(\underline{r}_1 \ldots \underline{r}_N)} d\underline{r}_{s+1} \ldots d\underline{r}_N .$$

The normalization equation for $n_s(\underline{r}_1 \ldots \underline{r}_s)$ is

$$(2.14)\quad \int\cdots\int n_s(\underline{r}_1,\ldots\underline{r}_s)\, d\underline{r}_1\ldots d\underline{r}_s$$

$$= \sum_{N=s}^{\infty} \frac{N!}{(N-s)!} \int P_N^{(G)}(\underline{r},\underline{p})\, d^N\underline{r}\, d^N\underline{p}$$

$$= \left\langle \frac{N!}{(N-s)!} \right\rangle$$

B. The Pair Correlation Function.

The dimensionless s-body correlation function $g_s(\underline{r}_1,\ldots,\underline{r}_s)$ is defined by

$$(2.15)\quad n_s(\underline{r}_1,\ldots,\underline{r}_s) = n_1(\underline{r}_1)\cdots n_1(\underline{r}_s) g_s(\underline{r}_1,\ldots,\underline{r}_s)\ .$$

The above equations are valid for both crystals and fluids; we now specialize to the latter. For a uniform system, the one-body density, $n_1(\underline{r}_1)$ is a constant,

$$(2.16)\quad n_1(\underline{r}_1) = n = \lim_{\bar{N},V\to\infty} \frac{\bar{N}}{V} = \text{const.}$$

From (2.15) and (2.16), the two-body distribution, $n_2(\underline{r}_1,\underline{r}_2)$ becomes: $n_2(\underline{r}_1,\underline{r}_2) = n^2 g_2(\underline{r}_1,\underline{r}_2)$. Because of the isotropy (spatial translation - invariance) of the fluid, the function $g_2(\underline{r}_1,\underline{r}_2)$ depends only on $r = |\underline{r}_2-\underline{r}_1|$, and so:

$$n_2(\underline{r}_1,\underline{r}_2) = n^2 g(|\underline{r}_1-\underline{r}_2|) \quad (2.17)$$

The quantity $g(|\underline{r}_1-\underline{r}_2|)$ is known as the pair correlation function, or radial distribution function.

Inasmuch as $g(r)$ determines the thermodynamics, it is the principal quantity desired in the N-body problem of classical equilibrium statistical mechanics. From (2.14), $g(r)$ is asymptotic to unity, in the thermodynamic limit, except during a phase transition when N has a double peak.

The total energy, E, of a fluid of N-particles interacting pairwise with a potential $\phi(r)$ in the absence of external fields can be shown to be [1]

$$E = \frac{3}{2} NkT + \frac{N}{2} n \int_0^\infty \phi(r)\, g(r)\, 4\pi r^2\, dr \quad (2.18)$$

The pressure, P, is given in terms of the grand partition function:

$$\beta VP = \ln Z_G \quad (2.19)$$

In expressing P directly in terms of g(r), however, there exists both the virial pressure relation,

$$\frac{PV}{NkT} = 1 - \frac{n}{6kT} \int_0^\infty r\phi'(r)\, g(r)\, 4\pi r^2\, dr \quad (2.20)$$

and the compressibility formula [2],

$$(2.21) \qquad \frac{n}{\beta} k_T = 1 + n \int_0^\infty [g(r)-1]\, 4\pi r^2\, dr = [1- n \int_0^\infty c(r)\, 4\pi r^2 dr]^{-1} ,$$

in which k_T is the isothermal compressibility, given by

$$(2.22) \qquad k_T = \frac{1}{n}(\frac{\partial n}{\partial p})_T \; .$$

The quantity c(r) appearing in (2.21) is an additional correlation function to be discussed in Section III.

The pressures calculated from (2.20) and (2.21) will be identical if the exact g(r) is used. Otherwise, there will be a discrepancy between them which is a measure of the accuracy of the theory of the approximate g(r) used.

Especially appropriate in a first-order theory of the correlation function (e.g., see equations (4.4) and (4.11) below) is the approximation to the free energy F, written out through second order,

$$(2.23) \qquad F = F_0 + \frac{1}{2} nN \int_0^\infty \phi_1(r)\, g_0(r)\, 4\pi r^2\, dr + \frac{1}{4} nN \int_0^\infty \phi_1(r)\, g_1(r)\, 4\pi r^2\, dr ,$$

where F_0 is the hard core free energy. The energy E and pressure P then follow from the relations

$$(2.24) \qquad E = \frac{\partial}{\partial\beta} \beta F$$

and

$$(2.25) \qquad P = - \frac{\partial F}{\partial V} = - \frac{1}{\beta} \int \frac{\partial E}{\partial V}\, d\beta \; .$$

III. Integral Equations for the Pair Correlation Function.

We next proceed to examine the formal procedures by means of which integral equations for the radial distribution function are obtained [3]. These equations provide an approximate theory of $g(r)$ for the N-body problem.

A. Functional Taylor Expansion.

First, consider a regular functional [4] of degree N

$$F[y(t)] = k_0 + \sum_{n=1}^{N} \int_a^b \cdots \int_a^b k_n(t_1 \ldots t_n) y(t_1) \ldots y(t_n) \, dt_1 \ldots dt_n \tag{3.1}$$

where the kernel $k_n(t_1 \ldots t_n)$ is symmetric with respect to its n variables in the interval from a to b. This can be extended to an infinite series by letting $N \to \infty$, such that $F[y(t)]$ will be convergent and will correspond to a definite value when the norm of $y(t)$, e.g. $|y(t)| \equiv [\int_a^b y^2(t)\, dt]^{1/2}$ is less than some radius of convergence.

$$F[y(t)] = k_0 + \sum_{n=1}^{\infty} \int_a^b \cdots \int_a^b k_n(t_1 \ldots t_n) y(t_1) \ldots y(t_n) dt_1 .. dt_n \tag{3.2}$$

The variational derivative of (3.2) is

$$\frac{\delta F}{\delta y(t_1)} = k_1(t_1) + \sum_{n=2}^{\infty} n \int_a^b \cdots \int_a^b k_n(t_1 \ldots t_n) y(t_2) .. y(t_n) \, dt_2 \ldots dt_n . \tag{3.3}$$

Continuing to differentiate p-1 times,

$$(3.4)\quad \frac{\delta^p F}{\delta y(t_p)\ldots\delta y(t_1)} = p!\ k_p(t_1\ldots t_p)$$

$$+ \sum_{n=p+1}^{\infty} \frac{n!}{(n-p)!} \int_a^b\cdots\int_a^b k_n(t_1\ldots t_n)y(t_{p+1})\ldots y(t_n)dt_{p+1}\ldots dt_n .$$

Hence,

$$(3.5)\qquad \left.\frac{\delta^p F}{\delta y(t_p)\ldots\delta y(t_1)}\right|_{y=0} = p!k_p(t_1\ldots t_p)\ ,$$

the relation between the kernel $k_p(t_1\ldots t_p)$, and the functional $F[y(t)]$ which generates it.

The functional Taylor expansion can then be written

$$(3.6)\quad F[y(t)] = F[0] + \sum_{p=1}^{\infty} \frac{1}{p!} \int_a^b\cdots\int_a^b \left.\frac{\delta^p F}{\delta y(t_p)\ldots\delta y(t_1)}\right|_{y=0}$$

$$\cdot\ y(t_1)\ldots y(t_p)\ dt_1\ldots dt_p\ .$$

If y is a function of a vector $\underline{r}$, (3.6) then obtains for $F[y(\underline{r})]$. The formula (3.6) allows us to obtain expressions for the distribution functions and thermodynamic variables in nonuniform systems, about their uniform system values [5]. The non-uniformity can arise either from an applied external potential, or from a change in the density; $F[y(\underline{r})]$ is then expanded in terms of whichever function is chosen to be varied.

B. The Generating Functional.

We now recall [6] that Z_G is the generating functional for the complete set of s-body joint distributions, $n_s(\underline{r}_1,\ldots,\underline{r}_s)$, $(s = 1,2,3,\ldots)$ given in (2.13). First, it will be convenient to employ the notation (from (2.9) and (2.3))

$$(3.7) \qquad Z_G(0) = \sum_{N=0}^{\infty} \frac{z^N}{N!} \int\cdots\int e^{-\frac{\beta}{2}\sum\limits_{i\neq j=1}^{N}\phi(\underline{r}_i,\underline{r}_j)} \, d\underline{r}_1\ldots d\underline{r}_N$$

and

$$(3.8) \qquad Z_G(\gamma) = \sum_{N=0}^{\infty} \frac{z^N}{N!} \int\cdots\int e^{-\frac{\beta}{2}\sum\limits_{i\neq j=1}^{N}\phi(\underline{r}_i,\underline{r}_j)} \cdot e^{\sum\limits_{i=1}^{N}\gamma(\underline{r}_i)} \, d\underline{r}_1\ldots d\underline{r}_N$$

with the dimensionless $\gamma(\underline{r}_i) = -\beta U(\underline{r}_i)$, to denote the grand partition function in the absence and presence, respectively, of any applied external potential, U. Similarly, from (2.13),

$$(3.9) \quad n_s(\underline{r}_1\ldots\underline{r}_s) = \frac{1}{Z_G(0)} \sum_{N=s}^{\infty} \frac{z^N}{N-s!} \int\cdots\int e^{-\frac{\beta}{2}\sum\limits_{i\neq j=1}^{N}\phi(\underline{r}_i,\underline{r}_j)} \, d\underline{r}_{s+1}\ldots d\underline{r}_N$$

and

$$(3.10) \quad n_s(\underline{r}_1\ldots\underline{r}_s|\gamma) = \frac{1}{Z_G(\gamma)} \sum_{N=s}^{\infty} \frac{z^N}{N-s!} \int\cdots\int e^{-\frac{\beta}{2}\sum\limits_{i\neq j=1}^{N}\phi(\underline{r}_i,\underline{r}_j)} \cdot e^{\sum\limits_{i=1}^{N}\gamma(\underline{r}_i)} \, d\underline{r}_{s+1}\ldots d\underline{r}_N.$$

From (3.8),

$$(3.11) \quad \frac{\delta Z_G}{\delta\gamma(\underline{r}_1)} = \sum_{N=1}^{\infty} \frac{z^N}{N-1!} \int\cdots\int e^{-\frac{\beta}{2}\sum_{i\neq j=1}^{N}\phi(\underline{r}_i,\underline{r}_j)} \cdot e^{\sum_{i=1}^{N}\gamma(\underline{r}_i)} \, d\underline{r}_2\ldots d\underline{r}_N ,$$

so that

$$(3.12) \quad \frac{\delta Z_G}{\delta e^{\gamma(\underline{r}_1)}} = e^{-\gamma(\underline{r}_1)} \frac{\delta Z_G}{\delta\gamma(\underline{r}_1)} = e^{-\gamma(\underline{r}_1)} \sum_{N=1}^{\infty} \frac{z^N}{N-1!}$$

$$\cdot \int\cdots\int e^{-\frac{\beta}{2}\sum_{i\neq j=1}^{N}\phi(\underline{r}_i,\underline{r}_j)} + e^{\sum_{i=1}^{N}\gamma(\underline{r}_i)} \, d\underline{r}_2\ldots d\underline{r}_N$$

Differentiating a total of s-times, one finds

$$(3.13) \quad \frac{\delta^s Z_G}{\delta e^{\gamma(\underline{r}_s)}\ldots\delta e^{\gamma(\underline{r}_1)}} = e^{-\gamma(\underline{r}_1)} \ldots e^{-\gamma(\underline{r}_s)} \sum_{N=s}^{\infty} \frac{z^N}{N-s!}$$

$$\cdot\int\cdots\int e^{-\frac{\beta}{2}\sum_{i\neq j=1}^{N}\phi(\underline{r}_i,\underline{r}_j)} \; e^{\sum_{i=1}^{N}\gamma(\underline{r}_i)} \, d\underline{r}_{s+1}\ldots d\underline{r}_N$$

$$= e^{-\gamma(\underline{r}_1)} \ldots e^{-\gamma(\underline{r}_s)} \; Z_G(\gamma) \; n_s(\underline{r}_1\ldots\underline{r}_s|\gamma) \; .$$

From formula (3.13), we have, for s = 1:

$$(3.14) \quad n_1(\underline{r}_1|\gamma) = \frac{1}{Z_G(\gamma)} e^{\gamma(\underline{r}_1)} \frac{\delta Z_G}{\delta e^{\gamma(\underline{r}_1)}} = \frac{\delta}{\delta\gamma(\underline{r}_1)} \ln Z_G(\gamma) \; .$$

Next, $\frac{\delta n_1(\underline{r}_1|\gamma)}{\delta\gamma(\underline{r}_2)} = \frac{1}{Z_G(\gamma)} \; \frac{\delta^2 Z_G(\gamma)}{\delta\gamma(\underline{r}_2)\delta\gamma(\underline{r}_1)} - n_1(r_1|\gamma)n_1(\underline{r}_2|\gamma)$. But from (3.11), $\frac{1}{Z_G(\gamma)} \frac{\delta^2 Z_G(\gamma)}{\delta\gamma(\underline{r}_2)\delta\gamma(\underline{r}_1)} = n_2(\underline{r}_1,\underline{r}_2|\gamma) + n_1(\underline{r}_1|\gamma)\delta(\underline{r}_1-\underline{r}_2)$. Thus,

$$(3.15)\quad \frac{\delta n_1(\underline{r}_1|\gamma)}{\delta\gamma(\underline{r}_2)} = n_2(\underline{r}_1,\underline{r}_2|\gamma) - n_1(\underline{r}_1|\gamma)n_1(\underline{r}_2|\gamma)+n_1(\underline{r}_1|\gamma)\delta(\underline{r}_1-\underline{r}_2).$$

In general [7],

$$(3.16)\quad \frac{\delta n_q(\underline{r}_1,\ldots,\underline{r}_q|\gamma)}{\delta\gamma(\underline{r})} = n_{q+1}(\underline{r}_1,\ldots,\underline{r}_q,\underline{r}|\gamma)$$

$$+ n_q(\underline{r}_1,\ldots,\underline{r}_q|\gamma) \left[\sum_{i=1}^{q} \delta(\underline{r}_i-\underline{r}) - n_1(\underline{r}|\gamma)\right] .$$

From (3.7) and (3.8), it is useful to note the following

$$(3.17)\quad Z_G(0) = \sum_{N=0}^{\infty} \frac{z^N}{N!} Z_N(0) = \sum_{N=0}^{\infty} \frac{z^N}{N!} \int\cdots\int e^{-\frac{\beta}{2}\sum_{i\neq j=1}^{N} \phi(\underline{r}_i,\underline{r}_j)} d\underline{r}_1\ldots d\underline{r}_N$$

$$= \sum_{N=s}^{\infty} \frac{z^{N-s}}{N-s!} Z_{N-s}(0) = \sum_{N=s}^{\infty} \frac{z^{N-s}}{N-s!} \int\cdots\int e^{-\frac{\beta}{2}\sum_{i\neq j=s+1}^{N} \phi(\underline{r}_i,\underline{r}_j)} d\underline{r}_{s+1}\ldots d\underline{r}_N$$

and

$$(3.18)\quad Z_G(\gamma) = \sum_{N=0}^{\infty} \frac{z^N}{N!} Z_N(\gamma) = \sum_{N=0}^{\infty} \frac{z^N}{N!} \int\cdots\int e^{-\frac{\beta}{2}\sum_{i\neq j=1}^{N} \phi(\underline{r}_i,\underline{r}_j)}$$

$$\cdot e^{\sum_{i=1}^{N} \gamma(\underline{r}_i)} d\underline{r}_1\ldots d\underline{r}_N =$$

$$= \sum_{N=s}^{\infty} \frac{z^{N-s}}{N-s!} Z_{N-s}(\gamma) = \sum_{N=s}^{\infty} \frac{z^{N-s}}{N-s!} \int\cdots\int e^{-\frac{\beta}{2} \sum_{i\neq j=s+1}^{N} \phi(\underline{r}_i,\underline{r}_j)} \cdot e^{\sum_{i=s+1}^{N} \gamma(\underline{r}_i)} d\underline{r}_{s+1}\cdots d\underline{r}_N .$$

For s = 1, (3.9) and (3.10) yield

$$(3.19) \quad n_1(\underline{r}_1) = \frac{1}{Z_G(0)} \sum_{N=1}^{\infty} \frac{z^N}{N-1!} \int\cdots\int e^{-\frac{\beta}{2} \sum_{i\neq j=1}^{N} \phi(\underline{r}_i,\underline{r}_j)} d\underline{r}_2\cdots d\underline{r}_N$$

$$(3.20) \quad n_1(\underline{r}_1|\gamma) = \frac{1}{Z_G(\gamma)} \sum_{N=1}^{\infty} \frac{z^N}{N-1!} \int\cdots\int e^{-\frac{\beta}{2} \sum_{i\neq j=1}^{N} \phi(\underline{r}_i,\underline{r}_j)} \cdot e^{\sum_{i=1}^{N} \gamma(\underline{r}_i)} d\underline{r}_2\cdots d\underline{r}_N .$$

It is advantageous to relabel as follows.

$$(3.21) \quad n_1(\underline{r}_2) = \frac{1}{Z_G(0)} \sum_{N=2}^{\infty} \frac{z^{N-1}}{N-2!} \int\cdots\int e^{-\frac{\beta}{2} \sum_{i\neq j=2}^{N} \phi(\underline{r}_i,\underline{r}_j)} d\underline{r}_3\cdots d\underline{r}_N$$

$$(3.22) \quad n_1(\underline{r}_2|\gamma) = \frac{1}{Z_G(\gamma)} \sum_{N=2}^{\infty} \frac{z^{N-1}}{N-2!} \int\cdots\int e^{-\frac{\beta}{2} \sum_{i\neq j=2}^{N} \phi(\underline{r}_i,\underline{r}_j)} \cdot e^{\sum_{i=2}^{N} \gamma(\underline{r}_i)} d\underline{r}_3\cdots d\underline{r}_N ,$$

which can then be interpreted as the one-body density in an (N-1)-particle system with an external potential energy, $\sum_{i=2}^{N} \gamma(\underline{r}_i)$. Similarly,

$$(3.23)\ n_1(\underline{r}_s) = \frac{1}{Z_G(0)} \sum_{N=s}^{\infty} \frac{z^{N-s+1}}{N-s!} \int\cdots\int e^{-\frac{\beta}{2}\sum_{i\neq j=s}^{N}\phi(\underline{r}_i,\underline{r}_j)} d\underline{r}_{s+1}\cdots d\underline{r}_N$$

and

$$(3.24)\ n_1(\underline{r}_s|\gamma) = \frac{1}{Z_G(\gamma)} \sum_{N=s}^{\infty} \frac{z^{N-s+1}}{N-s!} \int\cdots\int e^{-\frac{\beta}{2}\sum_{i\neq j=s}^{N}\phi(\underline{r}_i,\underline{r}_j)} \cdot e^{\sum_{i=s}^{N}\gamma(\underline{r}_i)} d\underline{r}_{s+1}\cdots d\underline{r}_N$$

are the one-body densities in an (N-s+1)-particle system without and with, respectively, an external potential energy, $\sum_{i=s}^{N}\gamma(\underline{r}_i)$.

Furthermore, the non-uniform two-body distribution can be written

$$(3.25)\ n_2(\underline{r}_2,\underline{r}_3|\gamma) = \frac{1}{Z_G(\gamma)} \sum_{N=3}^{\infty} \frac{z^{N-1}}{N-3!} \int\cdots\int e^{-\frac{\beta}{2}\sum_{i\neq j=2}^{N}\phi(\underline{r}_i,\underline{r}_j)} \cdot e^{\sum_{i=2}^{N}\gamma(\underline{r}_i)} d\underline{r}_4\cdots d\underline{r}_N\ .$$

C. Bootstrap Operation

It is now possible to show [8] that there exists a relation between uniform and non-uniform distribution functions, provided that the applied external potential, γ, is of a special type, denoted by $\tilde{\gamma}$. In particular, $\tilde{\gamma}(\underline{r}_j)$ is the external potential created at $\underline{r}_j$ by fixing s-particles at the positions $\underline{r}_1,\ldots,\underline{r}_s$ and allowing the remaining (N-s)-particles to interact pairwise with the s-centers of force each sees, i.e.,

$$(3.26) \qquad \tilde{\gamma}(\underline{r}_i) = -\beta \sum_{j=1}^{s} \phi(\underline{r}_j,\underline{r}_i)$$

is the external potential energy of a particle at $\underline{r}_j$. For instance, from (3.24)

$$(3.27)\ n_1(\underline{r}_{s+1}|\tilde{\gamma}(\underline{r}_{s+1})) = \frac{1}{Z_G(\tilde{\gamma})} \sum_{N=s+1}^{\infty} \frac{z^{N-s}}{N-(s+1)!} \int\cdots\int e^{-\frac{\beta}{2}\sum_{i\neq j=s+1}^{N}\phi(\underline{r}_i,\underline{r}_j)}\, e^{\sum_{i=s+1}^{N}\tilde{\gamma}(\underline{r}_i)}\, d\underline{r}_{s+2}\cdots d\underline{r}_N\ ,$$

where, from (3.18)

$$(3.28)\ Z_G(\tilde{\gamma}) = \sum_{N=s}^{\infty} \frac{z^{N-s}}{N-s!} \int\cdots\int e^{-\frac{\beta}{2}\sum_{i\neq j=s+1}^{N}\phi(\underline{r}_i,\underline{r}_j)}\, e^{\sum_{i=s+1}^{N}\tilde{\gamma}(\underline{r}_i)}\, d\underline{r}_{s+1}\cdots d\underline{r}_N\ .$$

The quantity $n_1(\underline{r}_{s+1}|\tilde{\gamma}(\underline{r}_{s+1}))$ is the one-body density in an (N-s)-particle system, with an external potential $\tilde{\gamma}$ created by fixing particles at $\underline{r}_1,\ldots,\underline{r}_s$.

An important special case occurs when only a single particle is fixed, at $\underline{r}_1$. Then, putting s = 1 in (3.26)-(3.28) gives

$$(3.29)\quad n_1(\underline{r}_2|\tilde{\gamma}(\underline{r}_2))$$

$$= \frac{\sum_{N=2}^{\infty} \frac{z^{N-1}}{N-2!} \int\cdots\int e^{-\frac{\beta}{2}\sum_{i\neq j=2}^{N}\phi(\underline{r}_i,\underline{r}_j)}\, e^{\sum_{i=2}^{N}\tilde{\gamma}(\underline{r}_i)}\, d\underline{r}_3\ldots d\underline{r}_N}{\sum_{N=1}^{\infty} \frac{z^{N-1}}{N-1!} \int\cdots\int e^{-\frac{\beta}{2}\sum_{i\neq j=2}^{N}\phi(\underline{r}_i,\underline{r}_j)}\, e^{\sum_{i=2}^{N}\tilde{\gamma}(\underline{r}_i)}\, d\underline{r}_2\ldots d\underline{r}_N}$$

with

$$(3.30)\qquad \tilde{\gamma}(\underline{r}_i) = -\beta\phi(\underline{r}_1,\underline{r}_i)\ .$$

The function $n_1(r_2|\tilde{\gamma}(\underline{r}_2))$ is the one-body density in an (N-1)-particle system, with an external potential $\tilde{\gamma}$ created by fixing one particle at $\underline{r}_1$. Because of the interaction between the fixed particle and the remaining particles, the density about the fixed particle is nonuniform. In this sense, the distribution of matter about a fixed particle can be thought of as the response of a system to an "external" field, $\tilde{\gamma}$. Also, from (3.25)

$$(3.31)\quad n_2(\underline{r}_2,\underline{r}_3|\tilde{\gamma}) = \frac{1}{Z_G(\tilde{\gamma})} \sum_{N=3}^{\infty} \frac{z^{N-1}}{N-3!} \int\cdots\int e^{-\frac{\beta}{2}\sum_{i\neq j=2}^{N}\phi(\underline{r}_i,\underline{r}_j)} \cdot e^{\sum_{i=2}^{N}\tilde{\gamma}(\underline{r}_i)} \, d\underline{r}_4\ldots d\underline{r}_N \ ,$$

with $\tilde{\gamma}(\underline{r}_i)$ given by (3.30).

Now, in addition to the ability to introduce the potential $\tilde{\gamma}$ in which fixed particles play a special role, another consequence of the procedure of setting aside fixed coordinate locations $\underline{r}_1,\ldots,\underline{r}_s$ is that conditional probability distributions are introduced into the interpretation. That is, "fixing" particles is a formal device which allows conditional distribution functions to be introduced [9]. For instance, the one-body density $n_1(\underline{r}_2|\tilde{\gamma}(\underline{r}_2))$ is merely the probability density, $p_2(\underline{r}_2|\underline{r}_1)$, of finding a particle at $\underline{r}_2$ when it is known that there is a particle at $\underline{r}_1$. That is, by fixing a particle at $\underline{r}_1$, the one-body distribution $n_1(\underline{r}_2|\tilde{\gamma}(\underline{r}_2))$ becomes a conditional two-body distribution

$$(3.32)\qquad n_1(\underline{r}_2|\tilde{\gamma}(\underline{r}_2)) = p_2(\underline{r}_2|\underline{r}_1) \ .$$

These conditional distributions provide the connection between uniform distributions and non-uniform distributions, viz., with $\tilde{\gamma}$ turned on. Thus, from (3.9)

$$(3.33)\quad \frac{n_2(\underline{r}_1,\underline{r}_2)}{n_1(\underline{r}_1)} = \frac{\sum_{N=2}^{\infty} \frac{z^{N-1}}{N-2!} \int\cdots\int e^{-\frac{\beta}{2}\sum_{i\neq j=1}^{N}\phi(\underline{r}_i,\underline{r}_j)} d\underline{r}_3\ldots d\underline{r}_N}{\sum_{N=1}^{\infty} \frac{z^{N-1}}{N-1!} \int\cdots\int e^{-\frac{\beta}{2}\sum_{i\neq j=1}^{N}\phi(\underline{r}_i,\underline{r}_j)} d\underline{r}_2\ldots d\underline{r}_N}$$

having multiplied both numerator and denominator by z^{-1}.

But $e^{-\frac{\beta}{2}\sum_{i\neq j=1}^{N}\phi(\underline{r}_i,\underline{r}_j)} = e^{-\frac{\beta}{2}\sum_{i\neq j=2}^{N}\phi(\underline{r}_i,\underline{r}_j)} \cdot e^{-\beta\sum_{i=2}^{N}\phi(\underline{r}_1,\underline{r}_i)}$.

Fix one particle at $\underline{r}_1$. Then, from (3.30)

$$(3.34)\quad \frac{n_2(\underline{r}_1,\underline{r}_2)}{n_1(\underline{r}_1)} = \frac{\sum_{N=2}^{\infty} \frac{z^{N-1}}{N-2!} \int\cdots\int e^{-\frac{\beta}{2}\sum_{i\neq j=2}^{N}\phi(\underline{r}_i,\underline{r}_j)}\, e^{\sum_{i=2}^{N}\tilde{\gamma}(\underline{r}_i)} d\underline{r}_3\ldots d\underline{r}_N}{\sum_{N=1}^{\infty} \frac{z^{N-1}}{N-1!} \int\cdots\int e^{-\frac{\beta}{2}\sum_{i\neq j=2}^{N}\phi(\underline{r}_i,\underline{r}_j)}\, e^{\sum_{i=2}^{N}\tilde{\gamma}(\underline{r}_i)} d\underline{r}_2\ldots d\underline{r}_N}$$

Direct comparison with (3.29) reveals that

$$(3.35)\qquad \frac{n_2(\underline{r}_1,\underline{r}_2)}{n_1(\underline{r}_1)} = n_1(\underline{r}_2|\tilde{\gamma}(\underline{r}_2)) .$$

A corresponding relation may be obtained for s-centers of force at $\underline{r}_1,\ldots,\underline{r}_s$. Thus, again from (3.9)

$$(3.36)\quad \frac{n_{s+1}(\underline{r}_1,\ldots,\underline{r}_{s+1})}{n_s(\underline{r}_1,\ldots,\underline{r}_s)} =$$

$$= \frac{\sum\limits_{N=s+1}^{\infty} \frac{z^{N-s}}{N-(s+1)!} \int\cdots\int e^{-\frac{\beta}{2}\sum\limits_{i\neq j=1}^{N}\phi(\underline{r}_i,\underline{r}_j)} \, d\underline{r}_{s+2}\ldots d\underline{r}_N}{\sum\limits_{N=s}^{\infty} \frac{z^{N-s}}{N-s!} \int\cdots\int e^{-\frac{\beta}{2}\sum\limits_{i\neq j=1}^{N}\phi(\underline{r}_i,\underline{r}_j)} \, d\underline{r}_{s+1}\ldots d\underline{r}_N}$$

having multiplied both numerator and denominator by z^{-s}.

But $e^{-\frac{\beta}{2}\sum\limits_{i\neq j=1}^{N}\phi(\underline{r}_i,\underline{r}_j)} = e^{-\frac{\beta}{2}\sum\limits_{i\neq j=s+1}^{N}\phi(\underline{r}_i,\underline{r}_j)}$

$\cdot e^{-\beta\sum\limits_{i=s+1}^{N}\sum\limits_{j=1}^{s}\phi(\underline{r}_j,\underline{r}_i)} \cdot e^{-\frac{\beta}{2}\sum\limits_{i\neq j=1}^{s}\phi(\underline{r}_i,\underline{r}_j)}$. Fix s-particles at $\underline{r}_1,\ldots,\underline{r}_s$. Then, from (3.26)

$$(3.37)\quad \frac{n_{s+1}(\underline{r}_1,\ldots,\underline{r}_{s+1})}{n_s(\underline{r}_1,\ldots,\underline{r}_s)}$$

$$= \frac{\sum\limits_{N=s+1}^{\infty} \frac{z^{N-s}}{N-(s+1)!} \int\cdots\int e^{-\frac{\beta}{2}\sum\limits_{i\neq j=s+1}^{N}\phi(\underline{r}_i,\underline{r}_j)} \, e^{\sum\limits_{i=s+1}^{N}\tilde{\gamma}(\underline{r}_i)} \, d\underline{r}_{s+2}\ldots d\underline{r}_N}{\sum\limits_{N=s}^{\infty} \frac{z^{N-s}}{N-s!} \int\cdots\int e^{-\frac{\beta}{2}\sum\limits_{i\neq j=s+1}^{N}\phi(\underline{r}_i,\underline{r}_j)} \, e^{\sum\limits_{i=s+1}^{N}\tilde{\gamma}(\underline{r}_i)} \, d\underline{r}_{s+1}\ldots d\underline{r}_N}$$

The factor $e^{-\frac{\beta}{2}\sum\limits_{i\neq j=1}^{s}\phi(\underline{r}_i,\underline{r}_j)}$, which represents the pairwise interaction of the s-centers of force among themselves, has cancelled out.

Comparing the right hand side of (3.37) and (3.27) indicates that

$$(3.38)\qquad \frac{n_{s+1}(\underline{r}_1,\ldots,\underline{r}_{s+1})}{n_s(\underline{r}_1,\ldots,\underline{r}_s)} = n_1(\underline{r}_{s+1}|\tilde{\gamma}(\underline{r}_{s+1}))$$

The one-body distribution with s-particles fixed at $\underline{r}_1,\ldots,\underline{r}_s$ is a conditional (s+1)-body distribution, $p_{s+1}(\underline{r}_{s+1}|\underline{r}_1,\ldots,\underline{r}_s)$

$$(3.39)\qquad n_1(\underline{r}_{s+1}|\tilde{\gamma}(\underline{r}_{s+1})) = p_{s+1}(\underline{r}_{s+1}|\underline{r}_1,\ldots,\underline{r}_s) .$$

In the first order approximate theory of the pair correlation function, it is necessary to fix only one particle; thus (3.35) is the equation which will be utilized.

The significance of (3.38) and (3.35) is that they enable higher-order distribution functions to be evaluated in terms of lower-order ones when the potential $\tilde{\gamma}$ is turned on; that is, they offer a "bootstrap" operation [10].

At this point we remark that the external potential γ employed in deducing formula (3.13) could have been $\tilde{\gamma}$; the same result would follow with suitable labelling to designate the locations of the fixed centers of force. In particular, the relation (3.15), in the presence of a single center of force at $\underline{r}_1$, could be written

$$(3.40)\qquad \frac{\delta n_1(\underline{r}_2|\tilde{\gamma}(\underline{r}_2))}{\delta\tilde{\gamma}(\underline{r}_3)} = n_2(\underline{r}_2,\underline{r}_3|\tilde{\gamma}) - n_1(\underline{r}_2|\tilde{\gamma})n_1(\underline{r}_3|\tilde{\gamma}) + n_1(\underline{r}_2|\tilde{\gamma})\delta(\underline{r}_2-\underline{r}_3) ,$$

in which (refer to (3.14))

$$(3.41)\qquad \begin{aligned} n_1(\underline{r}_2|\tilde{\gamma}(\underline{r}_2)) &= \frac{1}{Z_G(\tilde{\gamma})}\ \frac{\delta Z_G(\tilde{\gamma})}{\delta\tilde{\gamma}(\underline{r}_2)} \ , \\ n_1(\underline{r}_3|\tilde{\gamma}(\underline{r}_3)) &= \frac{1}{Z_G(\tilde{\gamma})}\ \frac{\delta Z_G(\tilde{\gamma})}{\delta\tilde{\gamma}\ (\underline{r}_3)} \ , \end{aligned}$$

with

$$(3.42)\quad \tilde{\gamma}(\underline{r}_2) = -\beta\phi(\underline{r}_1,\underline{r}_2)\ , \quad \tilde{\gamma}(\underline{r}_3) = -\beta\phi(\underline{r}_1,\underline{r}_3)\ .$$

D. Integral Equations

1. The Direct Correlation Function.

The formulas (3.6), (3.35), and (3.40) enable various integral equations for the pair correlation function to be obtained. First, suppose the function to be varied is the applied external potential, and that the one-body density is expanded as $\tilde{\gamma}$ is turned on. Then, from (3.6)

$$(3.43)\qquad n_1(\underline{r}|\tilde{\gamma}) = n + \int \left.\frac{\delta n_1(\underline{r}|\tilde{\gamma})}{\delta\tilde{\gamma}(\underline{y})}\right|_{\tilde{\gamma}=0} \tilde{\gamma}(\underline{y})\, d\underline{y} + \cdots \ .$$

Turn on a particle at $\underline{x}$, for example. Then for fluids, $\tilde{\gamma}(\underline{r}) = -\beta\phi(\underline{r}-\underline{x})$, $\tilde{\gamma}(\underline{y}) = -\beta\phi(\underline{y}-\underline{x})$ a function of relative coordinate alone.

Equation (3.35) then implies

$$(3.44)\qquad n_1(\underline{r}|\tilde{\gamma}) = \frac{n_2(\underline{r}-\underline{x})}{n}\ , \qquad n_1(\underline{y}|\tilde{\gamma}) = \frac{n_2(\underline{y}-\underline{x})}{n}\ ,$$

by virtue of (2.16). Next, (3.40) can be used to write

$\dfrac{\delta n_1(\underline{r}|\tilde{\gamma})}{\delta\tilde{\gamma}(\underline{y})} = n_2(\underline{r},\underline{y}|\tilde{\gamma}) - n_1(\underline{r}|\tilde{\gamma})n_1(\underline{y}|\tilde{\gamma}) + n_1(\underline{r}|\tilde{\gamma})\delta(\underline{r}-\underline{y})$. Thus (3.43) becomes

$$(3.45) \quad \frac{n_2(\underline{r}-\underline{x})}{n} = n - \int [n_2(\underline{r}-\underline{y}) - n^2 + n\delta(\underline{r}-\underline{y})]\beta\phi(\underline{y}-\underline{x})\, d\underline{y} + \dots .$$

This as a Debye-Hückel equation [11], valid for weak potentials, $\phi(\underline{r})$. Upon Fourier transforming, (3.45) may be solved in the form

$$(3.46) \qquad (g-1)_{\underline{k}} = \frac{-\beta\phi_{\underline{k}}}{1 + n\beta\phi_{\underline{k}}}$$

Alternatively, if the density is varied instead of the external potential, a simpler indication of the degree of inhomogeneity will be given. It is thus necessary to evaluate the "inverse" derivative, $\dfrac{\delta\gamma(\underline{r}_1)}{\delta n_1(\underline{r}_2|\gamma)}$; the effect of a density change on any quantity in the system may then be found by means of the chain rule. Inspection of (3.15) suggests that $\dfrac{\delta\gamma(\underline{r}_1)}{\delta n_1(\underline{r}_2|\gamma)}$ should also be split into singular and non-local parts:

$$(3.47) \quad \frac{\delta\gamma(\underline{r}_1)}{\delta n_1(\underline{r}_2|\gamma)} = \frac{1}{n_1(\underline{r}_2|\gamma)}\,\delta(\underline{r}_1-\underline{r}_2) - C(\underline{r}_1,\underline{r}_2|\gamma) .$$

This then expresses $\delta\gamma/\delta n_1$ in terms of the dimensionless quantity C, which is called the direct correlation function. From the chain rule,

$$(3.48) \qquad \int \frac{\delta n_1(\underline{r}_1|\gamma)}{\delta\gamma(\underline{r}_2)} \frac{\delta\gamma(\underline{r}_2)}{\delta n_1(r_3|\gamma)} \, d\underline{r}_2 = \delta(\underline{r}_1-\underline{r}_3) \; .$$

Substituting (3.15) and (3.47) into (3.48) and dropping the explicit specification $|\gamma)$ yields

$$(3.49) \quad g(\underline{r}_1,\underline{r}_2) -1 - c(\underline{r}_1,\underline{r}_2) = \int n(\underline{r}_3)c(\underline{r}_1,\underline{r}_3)[g(\underline{r}_2,\underline{r}_3)-1]d\underline{r}_3 .$$

Equation (3.49) is an exact interrelation between g and c. When iterated, (3.49) becomes

$$(3.50) \quad g(\underline{r}_1,\underline{r}_2)-1 = c(\underline{r}_1,\underline{r}_2) + \int c(\underline{r}_1,\underline{r}_3)n(\underline{r}_3)c(\underline{r}_3,\underline{r}_2) \, d\underline{r}_3$$

$$+ \iint c(\underline{r}_1,\underline{r}_3)n(\underline{r}_3)c(\underline{r}_3,\underline{r}_4)n(\underline{r}_4)c(\underline{r}_4,\underline{r}_2) \, d\underline{r}_3 \, d\underline{r}_4 + \cdots .$$

The right hand side of (3.50) is the deviation of g from its non-interaction value of unity.

2. The Percus-Yevick Equation

For the case of rapidly varying or discontinuous potentials -- the extreme case would be a rigid sphere interaction with an infinite discontinuity -- then the functional Taylor expansion of $n_1(\underline{r}|\tilde{\gamma})e^{-\tilde{\gamma}(\underline{r})}$ with respect to $n_1(\underline{r}|\tilde{\gamma})$, when truncated at the linear term, will be quite accurate due to the effect of the smallness of the direct correlations in the higher terms. Thus, from (3.6)

$$(3.51)\quad n_1(\underline{r}|\tilde{\gamma})e^{-\tilde{\gamma}(\underline{r})} = n + \int \left.\frac{\delta n_1(\underline{r}|\tilde{\gamma})e^{-\tilde{\gamma}(\underline{r})}}{\delta n_1(\underline{y}|\tilde{\gamma})}\right|_{\substack{n_1(\underline{y})=n \\ (\tilde{\gamma}\,=\,0)}} \cdot[n_1(\underline{y}|\tilde{\gamma})-n]d\underline{y}.$$

Using (3.44) and (3.47), and choosing the origin as $\underline{x}$, yields

$$(3.52)\quad g(\underline{r})e^{\beta\phi(\underline{r})}-1 = n\int c(\underline{r}-\underline{r}')(g(\underline{r}')-1)\,d\underline{r}' .$$

However, for uniform systems ($\tilde{\gamma} = 0$), and (3.49) becomes

$$(3.53)\quad g(\underline{r})-1-c(\underline{r}) = n\int c(\underline{r}-\underline{r}')(g(\underline{r}')-1)\,d\underline{r}' ,$$

which is a general relation between g and c for a uniform system.

Thus, from (3.52) and (3.53), the approximation (3.51) can be expressed in the form

$$(3.54)\qquad c(\underline{r}) = (1-e^{\beta\phi(\underline{r})})\,g(\underline{r}) .$$

This is the Percus-Yevick approximation. Using (3.53) and (3.54) to eliminate $c(\underline{r})$ results in a single integral equation for $g(\underline{r})$,

$$(3.55)\quad g(\underline{r})e^{\beta\phi(\underline{r})} - 1 = n\int (g(\underline{r}-\underline{r}')-1)(1-e^{\beta\phi(\underline{r}')})\,g(\underline{r}')\,d\underline{r}' .$$

Equation (3.55) is known as the Percus-Yevick (P.Y.) equation [12]. Defining the correlation function $\tau(\underline{r}) = g(\underline{r})e^{\beta\phi(\underline{r})}$, and using the notation $e(\underline{r}) = \exp(-\beta\phi(\underline{r}))$, $f(\underline{r}) = e(\underline{r}) - 1$, (3.55) may be written

$$(3.56) \qquad \tau(\underline{r}) - 1 = n \int [\tau(\underline{r}-\underline{r}')e(\underline{r}-\underline{r}') - 1]\, \tau(\underline{r}')\, f(\underline{r}')\, d\underline{r}' ,$$

a nonlinear Faltung equation.

The quantities $e(\underline{r})$, $f(\underline{r})$, $g(\underline{r})$ and $c(\underline{r})$ have finite discontinuities at any separation at which $\phi(\underline{r})$ is discontinuous. However, $\tau(\underline{r})$ is always continuous. The relation between c, g, and τ in the P.Y. approximation is, from (3.54) and the definition of $\tau(\underline{r})$,

$$(3.57) \qquad c(\underline{r}) = g(\underline{r}) - \tau(\underline{r}) .$$

From (3.54), it is noted that the range of $c(\underline{r})$ is exactly that of the intermolecular potential $\phi(\underline{r})$, in the P.Y. approximation.

IV. The First-Order Perturbed P.Y. Equation

The nonlinear integral equation (3.56) has been solved exactly for the case of hard rods (one dimension) and hard spheres (three dimensions) [13]. That is, the potential $\phi(\underline{r})$ has the form

$$(4.1) \quad \phi = 0 \quad (|\underline{r}| > a) \, , \qquad \phi = \infty \quad (|\underline{r}| < a) \, ,$$

where a is the range of the potential. Denoting this type of potential by the symbol $\phi_0(\underline{r})$, we have $e_0(\underline{r}) = \exp(-\beta\phi_0(\underline{r}))$, $f_0(\underline{r}) = e_0(\underline{r}) - 1$, and the correlations $c_0(\underline{r})$, $g_0(\underline{r})$ and $\tau_0(\underline{r})$, related in the P.Y. approximation by

$$(4.2) \quad c_0(\underline{r}) = \tau_0(\underline{r}) f_0(\underline{r}) \, , \qquad g_0(\underline{r}) = \tau_0(\underline{r}) e_0(\underline{r}) \, .$$

It is now convenient to refer to (3.56), with the potential (4.1), as the hard core P.Y. equation, or zeroth-order P.Y. equation. Written out in terms of the zero subscripts,

$$(4.3) \quad \tau_0(\underline{r}) - 1 = n(\tau_0 e_0 - 1) * \tau_0 f_0 \, .$$

The pair correlation function g_0 can be expressed as a sum of nth - neighbor contributions, and the direct correlation c_0 (the negative of which continues g_0 into the hard core interior) is given by a low order polynomial, of degree one or three for the case of one or three dimensional hard cores. The difference, $g_0 - c_0$, gives τ_0. The explicit form of these functions will be written down in the subsequent development, when required.

Exact solutions of (3.56) for general potentials of arbitrary range have never been found. It is however, possible to make progress toward this goal by exploiting the fact that the solutions of the zeroth-order equation (4.3) are known. The appropriate course would be to perturb the nonlinear equation (3.56), and then attempt to solve exactly the resulting first-order perturbed equation.

We write the interaction potential $\phi(\underline{r})$ as a sum of two parts, the repulsive hard core potential $\phi_0(\underline{r})$, plus a tail potential $\phi_1(\underline{r})$, which can be of arbitrary range:

$$\phi(\underline{r}) = \phi_0(\underline{r}) + \phi_1(\underline{r}) \,, \tag{4.4}$$

where

$$\phi_1 = 0 \quad (|\underline{r}| < a) \,, \qquad \phi_1 \neq 0 \quad (|\underline{r}| > a) \,. \tag{4.5}$$

Since adding an infinite range attractive type of potential, ϕ_1, would certainly be expected to modify the effects of the short-range core potential, ϕ_0, it is of dubious value to regard ϕ_1 as being "small enough" to be a perturbation on ϕ_0.

The quantity occurring directly in (3.56) is not the potential $\phi(\underline{r})$, but its exponential, $e(\underline{r})$. This suggests the possibility of perturbing (3.56) in powers of the exponential of ϕ_1, rather than ϕ_1 itself. Indeed, since $e_0(\underline{r})$ is a unit step function, and $\exp(-\beta\phi_1(\underline{r}))$ approaches unity rapidly (particularly for $\phi_1(\underline{r})$'s which $\rightarrow 0$ rapidly as $|\underline{r}| \rightarrow \infty$), the quantity $e_1(\underline{r})$, where

$$(4.6) \qquad e_1(\underline{r}) = e(\underline{r}) - e_0(\underline{r}) = e_0(\underline{r})[\exp(-\beta\phi_1(\underline{r})) - 1]$$

can properly be regarded as a pointwise perturbation on $e_0(\underline{r})$ for either attractive or repulsive ϕ_1, if $-\varepsilon < \beta\phi_1 < \frac{1}{\varepsilon}$. Then, to first-order in this perturbation scheme,

$$(4.7) \qquad \tau(\underline{r}) = \tau_0(\underline{r}) + \tau_1(\underline{r})$$

in which $\tau_1(\underline{r})$ is the solution of the first-order perturbed P.Y. equation:

$$(4.8) \quad \tau_1(\underline{r}) = n(\tau_0 e_0 - 1) * (\tau_0 e_1 + \tau_1 f_0) + n(\tau_0 e_1 + \tau_1 e_0) * \tau_0 f_0 .$$

Equations representing successively higher orders of the perturbation can also be obtained; the ultimate justification for a first-order perturbation will be a test of the closeness of agreement between the results it yields and the exact results.

As opposed to the nonlinear (3.55) on (3.56), (4.8) is now a linear equation for $\tau_1(\underline{r})$, which may be cast in the form of a Fredholm integral equation

$$(4.9) \qquad \tau_1(\underline{r}) = n \int k(\underline{r},\underline{r}') \, \tau_1(\underline{r}') \, d\underline{r}' + F(\underline{r})$$

in which the kernel $k(\underline{r},\underline{r}')$ is given by

$$(4.10) \qquad \begin{aligned} k(\underline{r},\underline{r}') &= \tau_0(\underline{r}-\underline{r}')[e_0(\underline{r}')f_0(\underline{r}-\underline{r}') + e_0(\underline{r}-\underline{r}')f_0(\underline{r}')] - f_0(\underline{r}'), \\ &\text{and} \\ F(\underline{r}) &= n(\tau_0 e_0 - 1 + \tau_0 f_0) * \tau_0 e_1 . \end{aligned}$$

Clearly the above kernel is not a function of (r-r') alone, meaning that (4.9) is not a convolution equation. Consequently, immediate solution of (4.8) by transforming and inverting is unfortunately not possible, and the task of solving becomes non-trivial.

The P.Y. equation, perturbed to first-order, can alternatively be expressed in terms of $c_1(\underline{r})$ and $g_1(\underline{r})$, rather than $\tau_1(\underline{r})$, as is (4.8). To do this, first write, as in (4.7)

$$(4.11)\quad g(\underline{r}) = g_0(\underline{r}) + g_1(\underline{r}) \ , \qquad c(\underline{r}) = c_0(\underline{r}) + c_1(\underline{r}) \ .$$

Then, from (3.53),

$$(4.12)\quad g_1(\underline{r}) - c_1(\underline{r}) \;=\; n\, c_0 * g_1 + n\, c_1 * (g_0 - 1)$$

and from (3.54),

$$(4.13)\qquad c_1(\underline{r}) = g_0(\underline{r})e_1(\underline{r}) \ , \qquad (|\underline{r}| > a) \ .$$

Equations (4.12) and (4.13) are an expression of the first-order perturbed P.Y. equation.

V. Solution of First-Order Perturbed P.Y. Equation: One Dimension.

A. Conversion to a Differential Equation.

A considerable effort was devoted to obtaining a technique for the exact solution of the first-order perturbed P.Y. equation for general potentials of arbitrary range [14]. Each method devised, although interesting in itself, was invariably discovered to be deficient in some significant way. We shall not discuss these shortcomings here, but instead proceed to explain the successful technique finally developed. This latter technique is suitable for both non-polar and polar liquids.

1. Sth - Neighbor Structure of $\gamma(x)$ and $\Gamma(x)$.

We begin by observing that equation (4.12) can be written in the form

$$g_1(\underline{r}) = \Gamma * C_1 \tag{5.1}$$

where

$$\Gamma(\underline{r}) = (\delta(\underline{r}) + n(g_0-1)) * (\delta(\underline{r}) + n(g_0-1)) \ , \tag{5.2}$$

itself a Faltung, is yet to be calculated.
Equation (5.1) is verified by Fourier transforming (4.12),

$$\hat{g}_1(\underline{k}) - \hat{c}_1(\underline{k}) = n\ \hat{c}_0(\underline{k})\hat{g}_1(\underline{k}) + n\ \hat{c}_1(\underline{k})(\hat{g}_0-1)(\underline{k}) \ . \tag{5.3}$$

Rearranging,

$$\hat{g}_1(\underline{k}) = \frac{1 + n(\hat{g}_0-1)(\underline{k})}{1 - n\hat{c}_0(\underline{k})} \; \hat{c}_1(\underline{k}) \; . \tag{5.4}$$

But from (3.53),

$$1 + n(\hat{g}_0-1)(\underline{k}) = (1 - n\hat{c}_0(\underline{k}))^{-1} \; . \tag{5.5}$$

Thus, (5.4) may be written

$$\hat{g}_1(\underline{k}) = \hat{\Gamma}(\underline{k}) \; \hat{c}_1(\underline{k}) \; , \tag{5.6}$$

having denoted

$$\hat{\Gamma}(\underline{k}) = (1-n\hat{c}_0(\underline{k}))^{-2} = (1+n(\hat{g}_0-1)(\underline{k}))^{2} \; , \tag{5.7}$$

and (5.1) follows by transforming (5.6) back to coordinate space.

It is of interest to calculate first $\gamma(\underline{r})$, defined as

$$\gamma(\underline{r}) = \delta(\underline{r}) + n(g_0-1)(\underline{r}) \; . \tag{5.8}$$

In one dimension, the Fourier transform pair for $\gamma(x)$ and $\hat{\gamma}(k)$ is

$$\begin{aligned} \gamma(x) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-ikx} \, \hat{\gamma}(k) \, dk \\ \hat{\gamma}(k) &= \int_{-\infty}^{\infty} e^{ikx} \, \gamma(x) \, dx \; . \end{aligned} \tag{5.9}$$

From (5.8) and (5.5),

$$\gamma(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{e^{-ikx}}{1 - n\hat{c}_0(k)} \, dk \; . \tag{5.10}$$

For one dimensional hard cores, the explicit expression for the symmetric function $c_0(x)$ is found [13] from solution of (4.3) to be

$$(5.11)\qquad \begin{aligned} c_0(x) &= -\,Q_0^2(1-n|x|)\ , &\quad |x| < a \\ &= 0 \ , &\quad |x| > a \end{aligned}$$

where $Q_0 = (1-na)^{-1}$.

For such a one dimensional hard core fluid, the exact $c_0(x)$ can be shown [15] to have precisely the range a, so that (5.11) is not an approximation but is identical with the exact result.

Using (5.11), the quantity $1-n\hat{c}_0(k)$ is readily calculated to be

$$(5.12)\qquad 1 - n\hat{c}_0(k) = A_0(k) + A_+(k)\, e^{-ika} + A_-(k)e^{ika}\ ,$$

in which

$$(5.13)\qquad \begin{aligned} A_0(k) &= 1 + \frac{2(nQ_0)^2}{k^2} \\ A_+(k) &= \frac{nQ_0}{k}\, i - \frac{(nQ_0)^2}{k^2} \\ A_-(k) &= -\frac{nQ_0}{k}\, i - \frac{(nQ_0)^2}{k^2}\ , \end{aligned}$$

so that, from (5.10),

$$(5.14)\qquad \gamma(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{e^{-ikx}}{A_0(k) + A_+(k)e^{-ika} + A_-(k)e^{ika}}\, dk\ .$$

Since $(A_0 + A_+e^{-ika} + A_-e^{ika})$ is non-vanishing (see (5.21)) and a continuous periodic function of period 2π in the variable (ka), a Fourier series expansion can be performed

(5.15) $$(A_0(k) + A_+(k)e^{-ika} + A_-(k)e^{ika})^{-1} = \sum_{s=-\infty}^{\infty} \hat{G}_s(k)e^{-iska},$$

where the Fourier coefficients $\hat{G}_s(k)$ are determined from

(5.16) $$\hat{G}_s(k) = \frac{1}{2\pi} \int_0^{2\pi} \frac{e^{iska}}{A_0(k) + A_+(k)e^{-ika} + A_-(k)e^{ika}} d(ka) .$$

With the substitution $z = e^{ika}$, $\hat{G}_s(k)$ can be written as a contour integral around the unit circle.

(5.17) $$\hat{G}_s(k) = \frac{1}{2\pi i} \oint_{|z|=1} \frac{z^s}{(A_0 + A_- z + A_+ z^{-1})} \frac{dz}{z} .$$

Suppose $s \geq 0$. Then

(5.18) $$\hat{G}_s(k) = \frac{1}{2\pi i} \oint_{|z|=1} \frac{z^s}{(A_- z^2 + A_0 z + A_+)} dz .$$

For $s \leq 0$, it is necessary only to complex conjugate $\hat{G}_s(k)$, that is,

(5.19) $$\hat{G}_{-s}(k) = \overline{\hat{G}_s(k)} .$$

The poles of the integrand in (5.18) occur when $z = z_1$ and $z = z_2$, where

(5.20) $$z_1 = -\frac{A_0}{2A_-} + \frac{\sqrt{A_0^2 - 4A_- A_+}}{2A_-}$$
$$z_2 = -\frac{A_0}{2A_-} - \frac{\sqrt{A_0^2 - 4A_- A_+}}{2A_-} .$$

Inserting the values of A_0, A_-, and A_+ from (5.13) into the square root reveals that

$$\sqrt{A_0^2 - 4A_-A_+} = 1 \; . \tag{5.21}$$

Further use of (5.13) implies that

$$z_1 = \frac{1}{1 + i\,\frac{k}{nQ_0}} \quad , \qquad z_2 = 1 - i\,\frac{k}{nQ_0} \; . \tag{5.22}$$

One pole (that at z_1) is inside the unit circle, whereas the second pole is outside. Therefore, $\hat{G}_s(k) = 2\pi i \text{ Res } (z_1)$. There follows

$$\hat{G}_s(k) = z_1^s = \left(\frac{1}{1 + i\,\frac{k}{nQ_0}}\right)^s \; , \qquad (s \geq 0) \; . \tag{5.23}$$

And from (5.19),

$$\hat{G}_s(k) = \left(1 - i\,\frac{k}{nQ_0}\right)^s \; , \qquad (s \leq 0) \; . \tag{5.24}$$

From (5.14) and (5.15),

$$\gamma(x) = \sum_{s=-\infty}^{\infty} \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-ik(x+sa)}\, \hat{G}_s(k)\, dk \; , \tag{5.25}$$

or

$$\gamma(x) = \sum_{s=-\infty}^{\infty} G_s(x+sa) \; , \tag{5.26}$$

where $G_s(x) = 0$ for $s/x > 0$ (refer to discussion for $\Gamma_s''(x)$ following (5.37)).

Thus, the well-known conclusion [13] that $\gamma(x)$, and hence $g_0(x)$, is expressible as a sum of s^{th} - neighbor contributions.

Returning to equation (5.1) and the quantity $\Gamma(x) = \gamma * \gamma(x)$, it will now be shown that $\Gamma(x)$ also has an S^{th} - neighbor structure. Since $\hat{\Gamma}(k) = (\hat{\gamma}(k))^2$, we have, corresponding to (5.10),

$$\Gamma(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{e^{-ikx}}{(1 - n\hat{c}_0(k))^2} \, dk \; . \tag{5.27}$$

In view of (5.12),

$$\Gamma(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{e^{-ikx}}{(A_0(k) + A_+(k)e^{-ika} + A_-(k)e^{ika})^2} \, dk \; . \tag{5.28}$$

Analogous to (5.15), there follows

$$(A_0(k) + A_+(k)e^{-ika} + A_-(k)e^{ika})^{-2} = \sum_{s=-\infty}^{\infty} \hat{\Gamma}_s(k) \, e^{-iska} , \tag{5.29}$$

in which the Fourier coefficients $\hat{\Gamma}_s(k)$ are given by

$$\hat{\Gamma}_s(k) = \frac{1}{2\pi} \int_0^{2\pi} \frac{e^{iska}}{(A_0(k) + A_+(k)e^{-ika} + A_-(k)e^{ika})^2} \, d(ka) \; , \tag{5.30}$$

which may be written as a contour integral (choosing $s \geq 0$, for example)

$$\hat{\Gamma}_s(k) = \frac{1}{2\pi i} \oint_{|z|=1} \frac{z^{s+1}}{(A_- z^2 + A_0 z + A_+)^2} \, dz \; . \tag{5.31}$$

The (double) poles of the integrand of (5.31) occur again at z_1 and z_2, given by (5.22). Residue evaluation of (5.31) results in

$$(5.32)\qquad \hat{\Gamma}_s(k) = (s + 1 + 2\,\frac{n^2Q_0^2}{k^2})(1 + i\,\frac{k}{nQ_0})^{-s}\ , \quad (s \geq 0).$$

For $s \leq 0$, complex congugate $\hat{\Gamma}_s(k)$. Thus,

$$(5.33)\qquad \hat{\Gamma}_s(k) = (-\,s + 1 + 2\,\frac{n^2Q_0^2}{k^2})(1 - i\,\frac{k}{nQ_0})^{s}\ , \quad (s \leq 0).$$

From (5.28) and (5.29),

$$(5.34)\qquad \Gamma(x) = \sum_{s=-\infty}^{\infty} \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-ik(x+sa)}\,\hat{\Gamma}_s(k)\,dk\ ,$$

or

$$(5.35)\qquad \Gamma(x) = \sum_{s=-\infty}^{\infty} \Gamma_s(x+sa)\ , \quad \text{where } \Gamma_s(x) = 0 \text{ for } \frac{s}{x} > 0,$$

a sum of sth - neighbor contributions, which will now be examined in greater detail.

2. Evaluation of $\Gamma''(x)$.

From (5.32) and (5.33), it is seen that in addition to the poles of order s at $k = nQ_0i$ (for $s \geq 0$) and $k = -nQ_0i$ (for $s \leq 0$), there exists a double pole at $k = 0$. This latter pole is undesirable from several points of view, and will be avoided by considering instead $\Gamma''_s(x+sa)$. Thus, from (5.35),

$$(5.36)\qquad \Gamma''(x) = \sum_{s=-\infty}^{\infty} \Gamma''_s(x+sa)\ , \qquad (-\infty < x < \infty),$$

where

$$(5.37) \qquad \Gamma_s''(x+sa) = -\frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-ik(x+sa)}(k^2\,\hat{\Gamma}_s(k))\,dk\ ,$$

such that (5.32) is to be used for $s \geq 0$, and (5.33) for $s \leq 0$. To evaluate (5.37), the semicircular contour must be closed in the upper half plane if $(x+sa) < 0$, and closed in the lower half plane if $(x+sa) > 0$. Since the algebraic sign of s fixes the location of the pole, there will be an extended range of x for which a given $\Gamma_s''(x+sa)$ vanishes, becoming and remaining non-zero outside this range. In concise form,

$$(5.38) \qquad \Gamma_s''(x+sa) = 0\ , \quad s(x+sa) > 0\ , \quad -\infty < x < \infty\ .$$

$\Gamma''(x)$ is a symmetric function which is composed of an infinite number of distinct s^{th} - neighbor functions, $\Gamma_s''(x+sa)$. For $sa < |x| < (s+1)a$, $\Gamma''(x)$ is a finite sum of (s+1)-terms; this piecewise character is a computational asset.

The first few $\Gamma_s''(x+sa)$ involve only delta-functions and their derivatives, and can be written down immediately from (5.37),

$$(5.39) \qquad \begin{aligned} \Gamma_0''(x) &= -\,2n^2Q_0^2\ \delta(x) + \delta''(x) \\ \Gamma_1''(x) &= -\,2n^2Q_0^2\ \delta(x) - 2nQ_0\ \delta'(x) \\ \Gamma_{-1}''(x) &= -\,2n^2Q_0^2\ \delta(x) + 2nQ_0\ \delta'(x)\ . \end{aligned}$$

3. Correlation Function Inside the Hard Cores

It is now possible to convert equation (5.1) into a differential equation. Thus, suppose x lies within the range of the potential $(0 < x < a)$. Since $g_1(x)$ vanishes in this range, (5.1) can be written

$$\int_{-a}^{a} \Gamma(x-x')\, b_1(x')\, dx' = -\Delta(x) \qquad (0 < x < a), \tag{5.40}$$

where, from (4.13)

$$\Delta(x) = \int_{-\infty}^{\infty} \Gamma(x-x')\, g_0(x')\, e_1(x')\, dx' \tag{5.41}$$

$$b_1(x) = c_1(x) \quad (|x| < a)\ , \qquad b_1(x) = 0 \quad (|x| > a)\ .$$

Once $b_1(x)$ is determined, it is then possible to obtain $g_1(x)$ $(= \Gamma{*}b_1+\Delta(x))$, $x > a$.

Taking two derivatives of (5.40), and noting that the argument of $\Gamma''(x-x')$ in the b_1-integral has the range $-a < x-x' < 2a$, in which range Γ'' is composed solely of delta-functions (see (5.39)), leads to the deduction that

$$b_1''(x) - 2nQ_0 b_1'(a-x) - 2n^2Q_0^2[b_1(x) + b_1(a-x)] = -\Delta''(x), \tag{5.42}$$

a second-order, first-difference equation for $b_1(x)$, in which the primes denote derivatives with respect to the arguments. By letting $x \to a-x$, another second-order, first-difference equation is obtained for $b_1(a-x)$

(5.43) $b_1''(a-x) - 2nQ_0 b_1'(x) - 2n^2Q_0^2[b_1(x) + b_1(a-x)] = -\Delta''(a-x)$.

(5.42) and (5.43) are simultaneous differential equations for $b_1(x)$ and $b_1(a-x)$. With $D = \frac{d}{dx}$, these are

$$(5.44a,b)\quad \begin{aligned} (D^2-2n^2Q_0^2)b_1(x) + (2nQ_0D-2n^2Q_0^2)b_1(a-x) &= -D^2\Delta(x) \\ (-2nQ_0D-2n^2Q_0^2)b_1(x) + (D^2-2n^2Q_0^2)b_1(a-x) &= -D^2\Delta(a-x) \end{aligned}$$

Eliminating $b_1(a-x)$ results in a single differential equation of fourth order for $b_1(x)$, valid in the interval $0 < x < a$:

$$(5.45)\quad D^4 b_1(x) = (2n^2Q_0^2\Delta'' - \Delta^{iv})(x) - 2(n^2Q_0^2\Delta'' + nQ_0\Delta''')(a-x).$$

B. Solution of Differential Equation.

1. Reduction of Inhomogeneous Term.

Denoting the right-hand side of (5.45) by $F(x)$, there follows

$$(5.46)\quad b_1(x) = b_1(0) + b_1'(0)x + \frac{1}{2}b_1''(0)x^2 + \frac{1}{6}b_1'''(0)x^3 + \int_0^x\cdots\int_0^x F(x)\, d^4x\ .$$

$F(x)$ and each of the four constants of integration $b_1(0)$, $b_1'(0)$, $b_1''(0)$, and $b_1'''(0)$ depend on the tail potential, $\phi_1(x)$. Since (5.46) is valid for all x in the interval $0 < x < a$, these four constants must be determined identically for a fixed $\phi_1(x)$.

The process of reducing[†] the multiple integral in (5.46) generates another cubic polynomial in x. When this is combined with the cubic already appearing in (5.46) (before reduction of the multiple integral), it then follows that

$$(5.47)\quad b_1(x) = (2n^2Q_0^2-D^2)\int_0^x\int_0^x \Delta(x)\, d^2x - (2n^2Q_0^2-2nQ_0D)\int_a^{a-x}\int_a^x \Delta(x)\, d^2x + B_0 + B_1x + B_2x^2 + B_3x^3, \quad (0 < x < a),$$

and

$$(5.48)\quad b_1(a-x) = (2n^2Q_0^2-D^2)\int_0^{a-x}\int_0^x \Delta(x)\, d^2x - (2n^2Q_0^2+2nQ_0D)\int_a^x\int_a^x \Delta(x)\, d^2x + B_0 + B_1(a-x) + B_2(a-x)^2 + B_3(a-x)^3, \quad (0<x<a),$$

where the constants B_0, B_1, B_2 and B_3 have resulted from the reduction of (5.46), and must be determined identically for all x in the interval $0 < x < a$. However, before applying the boundary conditions on $b_1(x)$ to accomplish this, it is necessary to first determine whether the four B_j ($j=0,1,2,3$) are linearly independent. That is, although (5.45) is of fourth order, it resulted from two second-order, first-difference equations either of which implies the other when the symmetry of $b_1(x)$ is used; the fourth-order differential equation is equivalent to a second-order, first-difference equation for symmetric $b_1(x)$.

[†] The formula $\underbrace{\int_0^x\cdots\int_0^x}_{n \text{ times}} F(x)\, \underbrace{dx\ldots dx}_{n \text{ times}} = \frac{1}{(n-1)!}\int_0^x (x-\zeta)^{n-1} F(\zeta)\, d\zeta$ can be useful in this regard.

2. Linear Dependence of Integration Constants.

Thus, first substituting (5.47) and (5.48) into (5.44a), and then into (5.44b), and simplifying, yields respectively:

$$(5.49)\quad [-2n^4Q_0^4 \int_0^a (a-2x)\Delta(x)\,dx - 2n^3Q_0^3 \int_0^a \Delta(x)\,dx$$

$$+ B_2 - nQ_0(B_1+ 2aB_2 +3a^2B_3) - n^2Q_0^2(2B_0+aB_1+a^2B_2+ a^3B_3)]$$

$$+ x[3B_3+ 2nQ_0(B_2+3aB_3)+ n^2Q_0^2(2aB_2+ 3a^2B_3)]$$

$$- nQ_0x^2[3B_3 + nQ_0(2B_2+ 3aB_3)] = 0 , \quad (0 < x < a),$$

and

$$(5.50)\quad [-2n^4Q_0^4 \int_0^a (a-2x)\Delta(x)\,dx - 2n^3Q_0^3 \int_0^a \Delta(x)\,dx$$

$$+ (B_2+ 3aB_3)- nQ_0B_1- n^2Q_0^2(2B_0+ aB_1+ a^2B_2+ a^3B_3)] +$$

$$+ x[-3B_3 - 2nQ_0B_2 + n^2Q_0^2(2aB_2 + 3a^2B_3)]$$

$$- nQ_0x^2[3B_3 + nQ_0(2B_2 + 3aB_3)] = 0 , \qquad (0 < x < a).$$

Equating to zero the coefficient of each power of x in (5.49) and (5.50) furnishes six equations for the four B_j's. Only two of these equations are independent, not being implied by the others. Thus, there results a system of defect two, given by:

$$(5.51) \quad \begin{aligned} -2n^2Q_0^2B_0 - nQ_0(1+anQ_0)B_1 + (1-a^2n^2Q_0^2)B_2 + a(3-a^2n^2Q_0^2)B_3 &= A \\ 2nQ_0B_2 \quad + \quad 3(1+anQ_0)B_3 \quad &= 0 \end{aligned}$$

where

$$A = 2n^4Q_0^4 \int_0^a (a-2x)\ \Delta(x)\ dx + 2n^3Q_0^3 \int_0^a \Delta(x)\ dx .$$

Assigning B_1 and B_3 arbitrarily, B_0 and B_2 are then linear combinations of B_1 and B_3, given by

$$(5.52) \quad \begin{aligned} B_2 &= -\frac{3(1+anQ_0)}{2nQ_0}\ B_3 \\ B_0 &= -\frac{A}{2n^2Q_0^2} - \frac{(1+anQ_0)}{2nQ_0}\ B_1 - \frac{1}{2n^2Q_0^2}\Big[\frac{3}{2nQ_0}(1+anQ_0) \\ &\qquad \cdot(1-a^2n^2Q_0^2) - a(3-a^2n^2Q_0^2)\Big]B_3 , \\ &\qquad B_1,\ B_3,\ \text{arbitrary.} \end{aligned}$$

(5.47) thus contains two arbitrary constants, to be determined from the continuity conditions at the hard core boundary. It is written finally as

$$(5.53)\quad b_1(x) = 2n^2Q_0^2 \int_0^x (x-\zeta)\Delta(\zeta)\, d\zeta - 2n^2Q_0^2 \int_a^{a-x} (a-x-\zeta)\Delta(\zeta)\, d\zeta - 2nQ_0 \int_a^{a-x} \Delta(\zeta)\, d\zeta - \Delta(x) + B_0 + B_1x + B_2x^2 + B_3x^3 , \qquad (0 < x < a) .$$

(5.53) is the exact solution of (5.1) for $0 < x < a$.

3. Continuity Conditions at Hard-Core Boundary.

It can be shown directly from (4.8) that in one dimension $\tau_1(x)$ and its first derivative are continuous at $x = a$. In three dimensions, τ_1 and its first three derivatives are continuous at the hard core boundary. As a consequence,

$$(5.54a,b)\quad \begin{aligned} g_1(a^+) &= g_0e_1(a^+) - b_1(a^-) , \\ g_1'(a^+) &= (g_0e_1)'(a^+) - b_1'(a^-) . \end{aligned}$$

Eliminating the $g_1(a^+)$ and $g_1'(a^+)$ by combining (5.54a,b) with the basic equation (5.1) yields two equations, implicitly, for B_1, B_3. These are

$$(5.55a,b)\quad \begin{aligned} \int_{-a}^{a} \Gamma(a^+-x')b_1(x')\, dx' + \Delta(a^+) &= g_0e_1(a^+) - b_1(a^-;B_1,B_3) \\ \int_{-a}^{a} \Gamma'(a^+-x')b_1(x')\, dx' + \Delta'(a^+) &= (g_0e_1)'(a^+) - b_1'(a^-;B_1,B_3). \end{aligned}$$

Because of (5.55), it is now necessary to obtain $\Gamma(x)$ itself; thus far, only $\Gamma''(x)$ has been evaluated (refer to (5.37)).

Knowledge of $\Gamma(x)$ is also a requirement for calculating $g_1(x)$, once $b_1(x)$ has been obtained.

As shown in the Appendix,

$$(A.5)\quad \Gamma(x) = \delta(x) + 2nc_0(x) - 3n^2Q_0^2|x| + K\ , \quad (-2a < x < 2a),$$

with

$$(A.9)\quad K = an^2Q_0^2(6 - 6an + \frac{10}{3}a^2n^2 - a^3n^3)\quad .$$

Inserting $\Gamma(a^+-x')$ and $\Gamma'(a^+-x')$ from (A.5) into (5.55a,b), and explicitly reducing $(\Gamma * b_1)(a^+)$ and $(\Gamma' * b_1)(a^+)$ leads to

$$(5.56a)\quad 2[(K-3an^2Q_0^2-nQ_0)\int_0^a b_1(x',B_1,B_3)\ dx' - n^2Q_0^2\int_0^a x'b_1(x',B_1,B_3)\ dx'] = g_0e_1(a^+) - \Delta(a^+) - b_1(a^-,B_1,B_3)$$

and

$$(5.56b)\quad -4n^2Q_0^2\int_0^a b_1(x',B_1,B_3)\ dx' = (g_0e_1)'(a^+) - \Delta'(a^+) - b_1'(a^-,B_1,B_3)\ .$$

We next use (5.53) to calculate $b_1(a^-,B_1,B_3)$ and $b_1'(a^-,B_1,B_3)$, and then substitute these into (5.56). The result is

$$(5.57a)\quad 2[(K-3an^2Q_0^2-nQ_0)\int_0^a b_1(x)\ dx - n^2Q_0^2\int_0^a xb_1(x)\ dx] = -2n^2Q_0^2\int_0^a (a-2x)\Delta(x)\ dx - 2nQ_0\int_0^a \Delta(x)\ dx -$$

$$- \ell(a,nQ_0) - [a + k(a,nQ_0)]B_1 - [a^3 + 3a^2 k(a,nQ_0) + m(a,nQ_0)]B_3,$$

and

$$-4n^2Q_0^2 \int_0^a b_1(x)\,dx = -2nQ_0\,\Delta(0) - B_1 - [3a^2 + 6ak(a,nQ_0)]B_3, \tag{5.57b}$$

in which

$$\begin{aligned} k(a,nQ_0) &= -\frac{(1+anQ_0)}{2nQ_0} \\ \ell(a,nQ_0) &= -\frac{A}{2n^2Q_0^2} \\ m(a,nQ_0) &= -\frac{1}{2n^2Q_0^2}\Big[\frac{3}{2nQ_0}(1+anQ_0)(1-a^2n^2Q_0^2) \\ &\qquad - a(3-a^2n^2Q_0^2)\Big] \end{aligned} \tag{5.58}$$

With the help of (5.53), the integrals on the left-hand sides of (5.57a) and (5.57b) can be written

$$\begin{aligned} \int_0^a b_1(x)\,dx = \sigma_1(a,nQ_0) &- \int_0^a \Delta(x)\,dx \\ &+ 2nQ_0 \int_0^a x\Delta(x)\,dx \\ &+ n^2Q_0^2\Big[a^2 \int_0^a \Delta(x)\,dx - 2a\int_0^a x\,\Delta(x)\,dx\Big] \end{aligned} \tag{5.59}$$

and

$$\begin{aligned} \int_0^a x\,b_1(x)\,dx = \sigma_2(a,nQ_0) &- \int_0^a x\,\Delta(x)\,dx \\ &+ nQ_0 \int_0^a (2ax-x^2)\Delta(x)\,dx \\ &+ 2n^2Q_0^2\Big[\frac{a^3}{3}\int_0^a \Delta(x)\,dx - \frac{a^2}{2}\int_0^a x\,\Delta(x)\,dx - \\ &- \frac{a}{2}\int_0^a x^2\Delta(x)\,dx + \frac{1}{3}\int_0^a x^3\Delta(x)\,dx\Big]\ ; \end{aligned} \tag{5.60}$$

where

(5.61) $$\sigma_1(a,nQ_0) = a\ell(a,nQ_0) + [\frac{a^2}{2} + ak(a,nQ_0)]B_1 + [\frac{a^4}{4} + a^3k(a,nQ_0) + am(a,nQ_0)]B_3$$

(5.62) $$\sigma_2(a,nQ_0) = \frac{1}{2}a^2\ell(a,nQ_0) + [\frac{a^3}{3} + \frac{a^2}{2}k(a,nQ_0)]B_1 + [\frac{a^5}{5} + \frac{3}{4}a^4k(a,nQ_0) + \frac{a^2}{2}m(a,nQ_0)]B_3$$

4. Explicit Equations for the Two Arbitrary Constants.

Substituting (5.59) and (5.60) into (5.57a) and rearranging enables us to write

(5.63) $$h_{11}B_1 + h_{12}B_3 = R_1$$

with the notation

(5.64a) $$h_{11} = 2a(K-3an^2Q_0^2 - nQ_0)(\frac{a}{2} + k(a,nQ_0)) - 2a^2n^2Q_0^2(\frac{a}{3} + \frac{1}{2}k(a,nQ_0)) + a + k(a,nQ_0)$$

(5.64b) $$h_{12} = 2a(K-3an^2Q_0^2 - nQ_0)(\frac{a^3}{4} + a^2k(a,nQ_0) + m(a,nQ_0)) - 2a^2n^2Q_0^2(\frac{1}{2}m(a,nQ_0) + \frac{3}{4}a^2k(a,nQ_0) + \frac{a^3}{5}) + (a^3 + 3a^2k(a,nQ_0) + m(a,nQ_0))$$

(5.64c) $$R_1 = \psi_1 - \ell(a,nQ_0)[2a(K - 3an^2Q_0^2 - nQ_0) - a^2n^2Q_0^2 + 1]$$

$$
\begin{aligned}
(5.64\text{d})\quad \psi_1 = {} & [(2K-6an^2Q_0^2-2nQ_0)(1-a^2n^2Q_0^2) - 2nQ_0 \\
& - 2an^2Q_0^2 + \frac{4}{3}\, a^3n^4Q_0^4] \cdot \int_0^a \Delta(x)\, dx \\
& + [(2K-6an^2Q_0^2-2nQ_0)(2an^2Q_0^2-2nQ_0) + 2n^2Q_0^2+4an^3Q_0^3 \\
& - 2a^2n^4Q_0^4] \cdot \int_0^a x\, \Delta(x)\, dx - (2n^3Q_0^3+2an^4Q_0^4) \int_0^a x^2\Delta(x)\, dx \\
& + \frac{4}{3}\, n^4Q_0^4 \int_0^a x^3\, \Delta(x)\, dx \; .
\end{aligned}
$$

Substituting (5.59) into (5.57b) and rearranging leads to

$$(5.65)\qquad h_{21}B_1 + h_{22}B_3 = R_2 \; ,$$

where

$$(5.66\text{a})\quad h_{21} = 1 - 2a^2n^2Q_0^2 - 4an^2Q_0^2k(a,nQ_0)$$

$$
\begin{aligned}
(5.66\text{b})\quad h_{22} = {} & 3a(a+2k(a,nQ_0)) - 4a^3n^2Q_0^2\left(\frac{a}{4} + k(a,nQ_0)\right) \\
& - 4an^2Q_0^2m(a,nQ_0)
\end{aligned}
$$

$$(5.66\text{c})\quad R_2 = \psi_2 - 2nQ_0\Delta(0) + 4a\, n^2Q_0^2\ell(a,nQ_0)$$

$$
\begin{aligned}
(5.66\text{d})\quad \psi_2 = {} & - 4n^2Q_0^2 \int_0^a \Delta(x)\, dx + 8n^3Q_0^3 \int_0^a x\, \Delta(x)\, dx \\
& + 4n^4Q_0^4 \left[a^2 \int_0^a \Delta(x)\, dx - 2a \int_0^a x\, \Delta(x)\, dx\right] .
\end{aligned}
$$

Thus, we have manipulated (5.55a,b) into two simultaneous equations -- refer to (5.63) and (5.65) -- for B_1 and B_3, explicitly.

From (5.63) and (5.65), B_1 and B_3 are found to be

$$B_1 = \frac{h_{22}R_1 - h_{12}R_2}{h_{11}h_{22} - h_{12}h_{21}} \tag{5.67a}$$

$$B_3 = \frac{h_{11}R_2 - h_{21}R_1}{h_{11}h_{22} - h_{12}h_{21}} \tag{5.67b}$$

With $b_1(x)$ determined, $g_1(x)$ follows from

$$g_1(x) = \Gamma * b_1(x) + \Delta(x) \ , \qquad (x > a). \tag{5.68}$$

VI. Comparison with Exact Results.

To examine the validity of the first-order perturbation theory, we can avail ourselves of the fact that the exact correlation functions are known for a one-dimensional system of hard cores (see remark below equation (5.11)). What is therefore indicated is an evaluation of $b_1(x)$, given by equation (5.53), for the case of "extended hard cores", i.e., for $\phi_1(x)$ itself a hard core. Geometrically, this is a means of decreasing the excluded length by increasing the size of the cores while maintaining the density constant. Once $b_1(x)$ is evaluated, comparison can be made with exact statistical mechanics.

A. Extended Hard-Core Kernel

Before performing the calculation of $b_1(x)$ from (5.53), which is tedious, we present the following simple considerations for the purpose of obtaining a quick estimate.

Regarding extended hard cores as a perturbation about hard cores, the first-order change in direct correlation function, $\delta c(x)$, is given by

$$(6.1) \qquad \delta c(x) = \int_{-\infty}^{\infty} \Lambda(x,x')\, e_1(x')\, dx' \ ,$$

in which, for finite core extension from a to a+b,

$$e_1(x') = -1 \ , \quad a < |x'| < a+b \ ,$$

and the kernel $\Lambda(x,x')$ is to be determined. From (5.11),

$$(6.2)\qquad \delta c(x) = (1-n|x|)\left[\frac{\varepsilon(a-|x|)}{(1-na)^2} - \frac{\varepsilon(a+b-|x|)}{(1-n(a+b))^2} \right],$$

where $\varepsilon(x)$ is the unit step function,

$$(6.3)\qquad \begin{aligned} \varepsilon(x) &= 1, \quad x > 0 \\ &= 0, \quad x < 0 \end{aligned}$$

Thus, (6.1) may be written

$$(6.4)\qquad (1-n|x|)\left[\frac{\varepsilon(a-|x|)}{(1-na)^2} - \frac{\varepsilon(a+b-|x|)}{(1-n(a+b))^2} \right] = \\ = - \int_a^{a+b} \Lambda(x,x')\, dx' - \int_{-(a+b)}^{-a} \Lambda(x,x')\, dx' .$$

Since $\Lambda(x,x')$ is even in both x and x', it follows that

$$(6.5)\qquad - \int_a^{a+b} \Lambda(x,x')\, dx' = \tfrac{1}{2} (1-n|x|)\left[\frac{\varepsilon(a-|x|)}{(1-na)^2} - \frac{\varepsilon(a+b-|x|)}{(1-n(a+b))^2} \right],$$

from which

$$(6.6)\qquad \int_0^a \Lambda(x,x')\, dx' - \tfrac{1}{2} (1-n|x|) \frac{\varepsilon(a-|x|)}{(1-na)^2} = \text{constant}.$$

Differentiating (6.6) with respect to a yields

$$(6.7)\qquad \Lambda(x,a) - n(1-n|x|) \frac{\varepsilon(a-|x|)}{(1-an)^3} - \frac{1}{2} \frac{(1-n|x|)}{(1-na)^2}\, \delta(a-|x|) = 0;$$

and therefore the result for the extended hard-core kernel $\Lambda(x,x')$ is

$$(6.8) \quad \Lambda(x,x') = n(1-n|x|)\,\frac{\varepsilon(|x'|-|x|)}{(1-n|x'|)^3} + \frac{1}{2}\,\frac{\delta(|x'|-|x|)}{(1-n|x'|)} \,,$$

where $|x'| \leq \frac{1}{n}$.

We shall defer use of (6.8) until the last chapter, and proceed next to the evaluation of the first-order P.Y. correlation function (5.53) for a hard-core tail potential.

B. Calculation of $\Delta(x)$

We choose $\phi_1(x)$ to be a hard core potential over the interval $a < |x| < a+\Delta a$, with (extended) range $\Delta a < a$. For all other values of $|x|$, $\phi_1(x)$ is zero. Consider the interval $0 < x < a$, over which $b_1(x)$ is non-zero. We want to calculate $\Delta(x)$, defined as

$$(6.9) \qquad \Delta(x) = \int_{-\infty}^{\infty} \Gamma(x-x')\, g_0(x')\, e_1(x')\, dx' \,.$$

From (6.9),

$$(6.10) \quad \Delta(x) = \int_{a}^{a+\Delta a} [\Gamma(x-x') + \Gamma(x+x')]\, g_0(x')\, e_1(x')\, dx', \qquad (0 < x < a);$$

$e_1(x') = -1$ $(a < x' < a+\Delta a)$, and is zero otherwise, accounting for the truncated limits of integration in (6.10). For the arguments of Γ in (6.10), there is the implication

$$-(a+\Delta a) < (x-x') < 0, \quad \text{and} \quad a < (x+x') < 2a+\Delta a \; .$$

Thus, $|x-x'| < 2a$ for all x in the interval $0 < x < a$, and all x' in the range of ϕ_1; whereas, $(x+x')$ can exceed 2a when $x > (a-\Delta a)$. However, for its argument exceeding 2a, Γ is given by an expression different from that which obtains when its argument is less than 2a. Consequently, $\Delta(x)$ will have different functional forms for $0 < x < a-\Delta a$, and $a-\Delta a < x < a$. Systemization is achieved by changing variables in (6.10), yielding

$$(6.11) \quad \Delta(x) = \int_{x-a-\Delta a}^{x-a} \Gamma(y) g_0(x-y) e_1(x-y)\, dy$$

$$+ \int_{x+a}^{x+a+\Delta a} \Gamma(y)\, g_0(y-x)\, e_1(y-x)\, dy \;, \quad (0<x<a-\Delta a),$$

and

$$(6.12) \quad \Delta(x) = \int_{x-a-\Delta a}^{x-a} \Gamma(y)\, g_0(x-y)\, e_1(x-y)\, dy$$

$$+ \int_{x+a}^{2a} \Gamma(y) g_0(y-x) e_1(y-x) dy + \int_{2a}^{x+a+\Delta a} \Gamma(y) g_0(y-x) e_1(y-x) dy, \; (a-\Delta a<x<a).$$

The y-limits of integration in (6.11) and (6.12) determine which expression to use for $\Gamma(y)$, i.e., either

$$(A.5) \quad \Gamma(y) = \delta(y) + 2nc_0(y) + K - 3n^2Q_0^2|y|, \; (-2a<y<2a) \;,$$

or

$$(\text{B.7})\quad \Gamma(y) = \delta(y) + 2nc_0(y) + K + \frac{3}{2}n^2Q_0^2(|y-2a|-2|y|)$$

$$- 4nQ_0e^{-nQ_0(y-2a)} + n^2Q_0^2(y-2a)e^{-nQ_0(y-2a)}, \quad (2a<y<3a)$$

(as shown in Appendices A and B).

Consider first the interval $0 < x < a-\Delta a$. Since $c_0(y) = 0$ when $|y| > a$, the limits of integration in $\int_{x-a-\Delta a}^{x-a} c_0(y)g_0(x-y)\,dy$ will depend on whether $0 < x < \Delta a$, or $\Delta a < x < a-\Delta a$. If we choose $\Delta a < a/2$ (similar considerations obtain for $\Delta a > a/2$), there follows

$$(6.13)\quad \int_{x-a-\Delta a}^{x-a} c_0(y)g_0(x-y)\,dy = \begin{cases} \int_{-a}^{x-a} c_0(y)g_0(x-y)dy, & 0<x<\Delta a \\ \int_{x-a-\Delta a}^{x-a} c_0(y)g_0(x-y)dy, & \Delta a<x<a-\Delta a. \end{cases}$$

Consequently, $\Delta(x)$ will be a continuous function of x for $0 < x < a$, but will have different functional forms for each of the three intervals $0 < x < \Delta a$, $\Delta a < x < a-\Delta a$, and $a-\Delta a < x < a$ (such that $0 < \Delta a < a/2$). We denote these three expressions by $\Delta_1(x)$, $\Delta_2(x)$ and $\Delta_3(x)$, respectively.

From (6.11), we find (for extended hard cores)

$$(6.14)\quad \Delta_1(x) = -2n\int_{-a}^{x-a} c_0(y)g_0(x-y)\,dy - K\int_{x-a-\Delta a}^{x-a} g_0(x-y)\,dy$$

$$- 3n^2Q_0^2\int_{x-a-\Delta a}^{x-a} y\,g_0(x-y)\,dy - K\int_{x+a}^{x+a+\Delta a} g_0(y-x)dy$$

$$+ 3n^2Q_0^2\int_{x+a}^{x+a+\Delta a} y\,g_0(y-x)\,dy, \quad 0 < x < \Delta a$$

and

$$(6.15)\quad \Delta_2(x) = -2n\int_{x-a-\Delta a}^{x-a} c_0(y)g_0(x-y)\,dy - K\int_{x-a-\Delta a}^{x-a} g_0(x-y)dy$$

$$- 3n^2Q_0^2\int_{x-a-\Delta a}^{x-a} y\,g_0(x-y)\,dy - K\int_{x+a}^{x+a+\Delta a} g_0(y-x)dy$$

$$+ 3n^2Q_0^2\int_{x+a}^{x+a+\Delta a} y\,g_0(y-x)\,dy, \quad \Delta a < x < a-\Delta a .$$

Working out the integrals, substituting their values into (6.14) and (6.15), and simplifying leads to the result

$$(6.16)\quad \Delta_1(x) = C_1 + C_2x, \qquad 0 < x < \Delta a$$

with

$$(6.17)\quad \begin{aligned} C_1 &= (6anQ_0^2 + 6Q_0 - \frac{2K}{n}) + [-6n(a+\Delta a)Q_0^2 - 6Q_0 + \frac{2K}{n}]e^{-nQ_0\Delta a} \\ C_2 &= 2nQ_0^2 \end{aligned}$$

and

(6.18) $$\Delta_2(x) = \bar{B}_1 + \bar{B}_2 x\ , \qquad \Delta a < x < a-\Delta a$$

with

(6.19) $$\begin{aligned} \bar{B}_1 &= 2[(1+2an)Q_0^2 + 2Q_0 - \frac{K}{n}] - 2[(1+2n(a+\Delta a))Q_0^2 + 2Q_0 - \frac{K}{n}]e^{-nQ_0\Delta a} \\ \bar{B}_2 &= 2nQ_0^2(1 - e^{-nQ_0\Delta a})\ . \end{aligned}$$

From equation (6.12), after evaluating the integrals and rearranging terms, we obtain

(6.20) $$\begin{aligned} \Delta_3(x) = A_1 + A_2 x + A_3 e^{nQ_0(x-a)} + A_4 e^{-nQ_0(x-a)} \\ + A_5 x e^{-nQ_0(x-a)}\ , \qquad a-\Delta a < x < a \end{aligned}$$

with

(6.21) $$\begin{aligned} A_1 &= [2(1+2an)Q_0^2 + 4Q_0 - \frac{2K}{n}] \\ &\quad + [-(2+\frac{11}{2}an + \frac{5}{2}n\Delta a)Q_0^2 - \frac{5}{2}Q_0 + 2\frac{K}{n}]e^{-nQ_0\Delta a} \\ A_2 &= \frac{1}{2}nQ_0^2(4 - e^{-nQ_0\Delta a}) \\ A_3 &= \frac{Q_0}{4} \\ A_4 &= [\frac{1}{2}n(\Delta a - a)Q_0^2 - \frac{7}{4}Q_0]e^{-2nQ_0\Delta a} \\ A_5 &= \frac{1}{2}nQ_0^2 e^{-2nQ_0\Delta a}\ . \end{aligned}$$

It can be shown directly from (6.16), (6.18) and (6.20) that

(6.22) $$\begin{aligned} \Delta_1(x=\Delta a) &= \Delta_2(x=\Delta a)\ , \\ \Delta_2(x=a-\Delta a) &= \Delta_3(x=a-\Delta a)\ . \end{aligned}$$

We remark that for the hard core tail potential which we postulate over $a < |x| < a+\Delta a$, the first derivative of $\Delta(x)$, $0 < x < a$, does not have to be continuous. Indeed,

$$\begin{aligned} \Delta_2'(x=\Delta a^+) - \Delta_1'(x=\Delta a^-) &= -2nQ_0^2 e^{-nQ_0\Delta a} \\ \Delta_3'(x=a-\Delta a^+) - \Delta_2'(x=a-\Delta a^-) &= 4nQ_0^2 e^{-nQ_0\Delta a}. \end{aligned} \tag{6.23}$$

C. Calculation of Direct Correlation Function.

We are interested in obtaining $b_1(x)$ over the "middle" interval, $\Delta a < x < a-\Delta a$, since this interval is dominantly larger than the other two for Δa small, and also the comparison between the first-order theory and exact theory will be optimum.

Referring to (5.53), we work out the following integrals, for $\Delta a < x < a-\Delta a$:

$$\int_0^x \Delta(\zeta)\, d\zeta = \mu_0 + \mu_1 x + \mu_2 x^2 \tag{6.24a}$$

$$\int_0^x \zeta\Delta(\zeta)\, d\zeta = \bar{\mu}_0 + \bar{\mu}_2 x^2 + \bar{\mu}_3 x^3 \tag{6.24b}$$

$$\int_a^{a-x} \Delta(\zeta)\, d\zeta = \varepsilon_0 + \varepsilon_1 x + \varepsilon_2 x^2 \tag{6.24c}$$

$$\int_a^{a-x} \zeta\Delta(\zeta)\, d\zeta = \bar{\varepsilon}_0 + \bar{\varepsilon}_1 x + \bar{\varepsilon}_2 x^2 + \bar{\varepsilon}_3 x^3 , \tag{6.24d}$$

in which

(6.25a) $$\mu_0 = (\Delta a)\cdot C_1 + \frac{1}{2}(\Delta a)^2\cdot C_2 - (\Delta a)\overline{B}_1 - \frac{1}{2}(\Delta a)^2\overline{B}_2$$

(6.25b) $$\mu_1 = \overline{B}_1$$

(6.25c) $$\mu_2 = \frac{1}{2}\overline{B}_2$$

(6.25d) $$\overline{\mu}_0 = \frac{1}{2}(\Delta a)^2 C_1 + \frac{1}{3}(\Delta a)^3 C_2 - \frac{1}{2}(\Delta a)^2\overline{B}_1 - \frac{1}{3}(\Delta a)^3\overline{B}_2$$

(6.25e) $$\overline{\mu}_2 = \frac{1}{2}\overline{B}_1$$

(6.25f) $$\overline{\mu}_3 = \frac{1}{3}\overline{B}_2$$

(6.25g) $$\varepsilon_0 = (\Delta a)\overline{B}_1 + \frac{1}{2}[2a\Delta a - (\Delta a)^2]\overline{B}_2$$

$$+\left[\frac{-A_3}{nQ_0} + \frac{A_4}{nQ_0} + \frac{A_5}{n^2Q_0^2}(1+anQ_0)\right] - (\Delta a)(A_1+aA_2) + \frac{1}{2}(\Delta a)^2 A_2$$

$$+ \frac{A_3}{nQ_0}e^{-nQ_0\Delta a} - \left[\frac{A_4}{nQ_0} + \frac{A_5}{n^2Q_0^2}(1+anQ_0)\right]e^{nQ_0\Delta a} + \frac{(\Delta a)}{nQ_0}A_5 e^{nQ_0\Delta a}$$

(6.25h) $$\varepsilon_1 = -\overline{B}_1 - a\overline{B}_2$$

(6.25i) $$\varepsilon_2 = \frac{1}{2}\overline{B}_2$$

(6.25j) $$\overline{\varepsilon}_0 = \frac{1}{2}[2a\Delta a - (\Delta a)^2]\overline{B}_1 + \frac{1}{3}[3a^2\Delta a - 3a(\Delta a)^2 + (\Delta a)^3]\overline{B}_2$$

$$+ \frac{1}{n^2Q_0^2}\left[A_3(1-anQ_0) + A_4(1+anQ_0) + \frac{A_5}{nQ_0}(a^2n^2Q_0^2 + 2anQ_0 + 2)\right]$$

$$- a\Delta a(A_1+aA_2) + \frac{1}{2}(\Delta a)^2(A_1+2aA_2) - \frac{1}{3}(\Delta a)^3 A_2 \quad +$$

$$+ \frac{A_3}{n^2Q_0^2}(anQ_0-1)e^{-nQ_0\Delta a} - \frac{(\Delta a)}{nQ_0} A_3 e^{-nQ_0\Delta a}$$

$$- \frac{1}{n^2Q_0^2}[A_4(1+anQ_0) + \frac{A_5}{nQ_0}(a^2n^2Q_0^2 + 2anQ_0 + 2)]e^{nQ_0\Delta a}$$

$$+ \frac{(\Delta a)}{nQ_0}[A_4 + \frac{2A_5}{nQ_0}(1 + anQ_0)]e^{nQ_0\Delta a} - \frac{(\Delta a)^2}{nQ_0} A_5 e^{nQ_0\Delta a}$$

(6.25k) $$\bar{\varepsilon}_1 = -a\bar{B}_1 - a^2\bar{B}_2$$

(6.25l) $$\bar{\varepsilon}_2 = \frac{1}{2}\bar{B}_1 + a\bar{B}_2$$

(6.25m) $$\bar{\varepsilon}_3 = -\frac{1}{3}\bar{B}_2.$$

We now construct the quantity $b_1(x) - \sum_0^3 B_\ell x^\ell$ appearing in (5.53), for $\Delta a < x < a-\Delta a$. Using (6.24) there follows

(6.26) $$b_1(x) - \sum_0^3 B_\ell x^\ell = \sum_0^3 \nu_\ell x^\ell , \qquad \Delta a < x < a-\Delta a,$$

in which the B_ℓ are given by (5.52) and (5.67), and the ν_ℓ are merely

(6.27a) $$\nu_0 = -\bar{B}_1 - 2n^2Q_0^2\bar{\mu}_0 - 2nQ_0(1+anQ_0)\varepsilon_0 + 2n^2Q_0^2\bar{\varepsilon}_0$$

(6.27b) $$\nu_1 = -\bar{B}_2 + 2n^2Q_0^2\mu_0 + 2n^2Q_0^2\varepsilon_0 - 2nQ_0(1+anQ_0)\varepsilon_1 + 2n^2Q_0^2\bar{\varepsilon}_1$$

(6.27c) $$\nu_2 = 2n^2Q_0^2(\mu_1 - \bar{\mu}_2 + \varepsilon_1 - a\varepsilon_2 + \bar{\varepsilon}_2 - \frac{\varepsilon_2}{nQ_0})$$

(6.27d) $$\nu_3 = 2n^2Q_0^2(\mu_2 - \bar{\mu}_3 + \varepsilon_2 + \bar{\varepsilon}_3) .$$

By substituting from (6.25) and (6.19), and manipulating, (6.27c) and (6.27d) become, respectively

(6.28) $$\nu_2 = - 2n^2Q_0^3(1 + anQ_0)(1 - e^{-nQ_0\Delta a})$$

and

(6.29) $$\nu_3 = \frac{4}{3} n^3Q_0^4(1 - e^{-nQ_0\Delta a})$$

from which

(6.30) $$\frac{\nu_2}{\nu_3} = - \frac{3(1+anQ_0)}{2nQ_0}$$

Inspection of (5.52) enables us to deduce that

(6.31) $$\frac{\nu_2}{\nu_3} = \frac{B_2}{B_3}$$

But (6.31) is the necessary condition that $b_1(x)$ be linear for $\Delta a < x < a-\Delta a$ (refer to (6.26)), and strongly indicates this.

Thus, we conclude that the first-order theory here yields a straight line,

(6.32) $$b_1(x) = (\nu_0+B_0) + (\nu_1+B_1)x \ , \qquad \Delta a < x < a-\Delta a,$$

in accord with the exact theory, viz.,

(6.33) $$C_{exact}(x) = - Q^2(1-nx) \ , \qquad 0 < x < a+\Delta a$$

with

$$Q^{-1} = 1 - n(a + \Delta a) \ ,$$

and we are comparing the lines $b_1(x)$ versus $[C_{exact}(x) - c_0(x)]$ over $\Delta a < x < a-\Delta a$ (Δa small but finite).

The slopes and intercepts of $b_1(x)$ and $[c_{ex.}(x)-c_0(x)]$ are unequal, for finite Δa, but the interesting feature is that the first-order perturbed equation does yield the correct functional dependence (linear) over the interval $\Delta a < x < a-\Delta a$ of comparison with exact statistical mechanics. Even though this might be expected, as ϕ_1 is a replica of a potential known to provide a direct correlation function which is linear, its demonstration forthwith is reassuring and lends credence to our technique.

In the limit $\Delta a \to 0$, the slopes and intercepts of both $b_1(x)$ and $[c_{ex.}(x) - c_0(x)]$ approach zero, and in the same way. That is, $b_1'(\Delta a)$ equals $c_{ex.}'(\Delta a)$ as the replica sphere vanishes.

VII. Applications.

A. Hard Cores with Surface Adhesion.

The extended hard-core kernel, $\Lambda(x,x')$, of equation (6.8) can be used to obtain the first-order change in direct correlation function for the sticky hard-core ("glue") model of Baxter [16]. In this model, the potential consists of a hard core plus a rectangular attractive well for which a certain limit is taken to make the range of the well become zero and its depth infinite. This is the dual of the Kac model [17], in which the tail potential has infinite range and vanishing amplitude. Both models exhibit a first order phase transition when solved rigorously.

In the glue model,

$$(7.1) \qquad e_1^{(\mathrm{glue})}(x') = A[\delta(x'-a) + \delta(x'+a)]$$

where A is a normalization constant. From (6.1) and (6.8),

$$(7.2) \qquad \delta c^{\mathrm{glue}}(x) = \int_{-\infty}^{\infty} \Lambda(x,x')\, e_1^{\mathrm{glue}}(x')\, dx' .$$

Thus

$$(7.3) \qquad \delta c^{\mathrm{glue}}(x) = 2\, A\, \Lambda(x,a) .$$

Using (6.7), the result is

$$(7.4) \qquad \delta c^{\mathrm{glue}}(x) = 2AQ_0[-nc_0(x) + \tfrac{1}{2}\,\delta(a-|x|)] ,$$

with $Q_0 = (1-an)^{-1}$.

The expression (7.4) for $\delta c^{glue}(x)$ is of the same type as $(c^{(glue)}_{exact}(x) - c_0(x))$. From (2.21), there is the equation of state:

$$(7.5)\quad \frac{\partial}{\partial n} \beta P = 1 - n \int_{-\infty}^{\infty} c(x)\, dx = \frac{\partial}{\partial n} \beta P_0 - n \int_{-\infty}^{\infty} \delta c^{glue}(x)\, dx$$

where $\frac{\partial}{\partial n} \beta P_0$ is the hard core contribution, equal to Q_0^2. Substituting $\delta c^{glue}(x)$ from (7.4) into (7.5), we obtain

$$(7.6)\qquad \frac{\partial}{\partial n} \beta P = (1 - 2nAQ_0) \frac{\partial}{\partial n} \beta P_0 ,$$

with a van der Waals loop.

The use of $\Lambda(x,x')$ in (7.2) to obtain $\delta c^{glue}(x)$ is not merely ad hoc; this technique can also be applied to other short-range tail potentials. It is the restriction, $an \leq 1$, on the size a and density n of the cores which determines the scope of the method; the strong singularity of $\Lambda(x,x')$ at $|x'| = 1/n$ corresponds to close packing and consequently imposes a limitation on the range of the tail potentials which can be treated.

B. The Debye-Huckel Model with Hard Core Insertion.

In the previous chapter we established that $b_1(x)$ is linear for an extended hard core of finite range. Since the theory is linear in e_1, scaling arguments indicate that soft-core tail potentials also show a linear region for $b_1(x)$, over $0 < x < a$. Since arbitrary short-range $\phi_1(x)$'s can be composed approximately of incremental cores, it is expected that $b_1(x)$ will remain linear for such $\phi_1(x)$'s. For long range tails, however, such arguments cannot be sustained (the condition $an \leq 1$ would be violated).

However, if the phenomenon of linearity is extrapolated as a model for arbitrary tail potential, and the P.Y. equation is further simplified to the Debye-Huckel model with hard core insertion (extended mean spherical model [18,19]), a number of explicit solutions can be obtained.

The D.H. model with hard core insertion is defined by the following equations:

$$g(x) - 1 - c(x) = n(g-1) * c \ , \quad -\infty < x < \infty \tag{7.7a}$$

$$c(x) = -\beta\ \phi(x) \ , \qquad |x| > a \tag{7.7b}$$

$$g(x) = 0 \ , \qquad |x| < a \ . \tag{7.7c}$$

The existence of a hard core is indicated by (7.7c). This hybrid model is computationally simpler than the full P.Y. equation, and is useful now since one of the two unknowns, namely, $c(x)$ for $|x| < a$ (the other unknown is $g(x)$, for $|x| > a$) can be assumed linear as a result of the prior approximation that $c(x)$ in vicinity of origin is shielded from the explicit tail, and feels only the net pressure.

Thus, we write

$$c(x) = \alpha + \gamma x , \qquad 0 < x < a , \tag{7.8}$$

in which the constants α and γ are to be determined by the continuity conditions on c and g in this model. Thus, from (7.7a,c) for $y > 0$:

$$\begin{aligned} g(y) - c(y) = {} & \left(1 - 2n \int_0^\infty c(x)\, dx\right) + n \int_a^\infty c(x+y)\, g(x)\, dx \\ & + n \int_{a+y}^\infty c(x-y) g(x) dx + n \int_a^{a+y} c(x-y) g(x) dx. \end{aligned} \tag{7.9}$$

Differentiating (7.9), there follows

$$\begin{aligned} g'(y)-c'(y) = {} & n \int_a^\infty c'(x+y) g(x) dx - n \int_{a+y}^\infty c'(x-y) g(x) dx \\ & -nc(a^+) g(a+y) - n \int_a^{a+y} c'(x-y) g(x) dx + nc(a^-) g(a+y) , \end{aligned} \tag{7.10}$$

and

$$\begin{aligned} g''(y)-c''(y) = {} & n \int_a^\infty c''(x+y) g(x) dx + n \int_{a+y}^\infty c''(x-y) g(x) dx \\ & +nc'(a^+) g(a+y) - nc(a^+) g'(a+y) + n \int_a^{a+y} c''(x-y) g(x)\, dx \\ & - nc'(a^-) g(a+y) + n\, c(a^-)\, g'(a+y) . \end{aligned} \tag{7.11}$$

Thus, as y approaches zero, (7.9)-(7.11) take the form

$$-c(0^+) = (1 - 2n\int_0^\infty c(x)\,dx) + 2n\int_a^\infty c(x)g(x)\,dx \tag{7.12}$$

$$-c'(0^+) = n(c(a^-) - c(a^+))g(a^+) \tag{7.13}$$

$$-c''(0^+) = n(c(a^-) - c(a^+))g'(a^+) \tag{7.14}$$

$$- n(c'(a^-) - c'(a^+))g(a^+) + 2n\int_a^\infty c''(x)\,g(x)\,dx \;,$$

respectively. Since g-c and its first derivative are continuous at a, and $g(a^-) = g'(a^-) = 0$, we have

$$\begin{aligned} g(a^+) &= c(a^+) - c(a^-) \\ g'(a^+) &= c'(a^+) - c'(a^-)\;. \end{aligned} \tag{7.15}$$

Using (7.15), (7.12)-(7.14) simplify to

$$-c(0^+) = (1 - 2n\int_0^\infty c(x)\,dx) + 2n\int_a^\infty c(x)\,g(x)\,dx \tag{7.16}$$

$$-c'(0^+) = -n\,(c(a^+) - c(a^-))^2 \tag{7.17}$$

$$-c''(0^+) = 2n\int_a^\infty c''(x)\,g(x)\,dx\;. \tag{7.18}$$

It is noted that for no tail at all, $\phi = 0$, (7.16)-(7.18) correctly imply

(7.19a) $$-c_0(0^+) = 1 - 2n \int_0^\infty c_0(x)\, dx = Q_0^2$$

(7.19b) $$-c_0'(0^+) = -\, n\, Q_0^2$$

(7.19c) $$-c_0''(0^+) = 0 \ .$$

C. Long-Range Forces.

We now carry out an explicit solution for an attractive Yukawa tail potential.

The potential is

(7.20) $$\phi(x) = -\, A\, e^{-\lambda|x|} \ , \qquad \text{for } |x| > a.$$

From (7.7b),

(7.20') $$c(x) = \beta A\, e^{-\lambda|x|} \ , \qquad |x| > a.$$

Clearly,

(7.21) $$c''(x) - \lambda^2 c(x) = 0 \ , \qquad |x| > a.$$

It follows from (7.8) that

(7.22) $$c(0) = \alpha \ , \quad c'(0) = \gamma \ , \quad c''(0) = 0 \ .$$

By means of (7.18), (7.21) and (7.22) we find

(7.23) $$\int_a^\infty c''(x)\, g(x)\, dx = 0 \ ; \qquad \int_a^\infty c(x)\, g(x)\, dx = 0 \ .$$

Using (7.8) and (7.20') indicates that

$$c(a^-) = \alpha + a\gamma \;, \quad c(a^+) = \beta A\, e^{-\lambda a} \;, \tag{7.24}$$

and

$$\int_0^\infty c(x)\, dx = \alpha a + \frac{1}{2}\gamma a^2 + \frac{\beta A}{\lambda} e^{-\lambda a} \;. \tag{7.25}$$

Substituting (7.22), (7.24) and (7.25) into (7.16) and (7.17) yields two equations for α and γ :

$$-\alpha = 1 - 2n(\alpha a + \frac{1}{2}\gamma a^2 + \frac{\beta A}{\lambda} e^{-\lambda a}) \tag{7.26a}$$

$$\gamma = n(\alpha + a\gamma - \beta A\, e^{-\lambda a})^2 \;. \tag{7.26b}$$

Referring to (2.21), (2.22), (7.16), (7.22) and (7.23), there exists the relation

$$\frac{\partial}{\partial n}(\beta P) = \frac{\beta}{n} k_T^{-1} = 1 - 2n \int_0^\infty c(x)\, dx = -c(0) = -\alpha \;. \tag{7.27}$$

Equations (7.26a,b) can be solved readily. First, from (7.26a), we have

$$a\gamma = (\frac{1}{a\,n} - \frac{2\ \beta A}{a\lambda} e^{-\lambda a}) + \alpha(\frac{1}{an} - 2) \;. \tag{7.28}$$

Substituting (7.28) into (7.26b) in order to eliminate γ leads to the following quadratic equation for α :

$$p\alpha^2 + q\alpha + r = 0 \tag{7.29}$$

with

$$p = (1 - an)^2$$

(7.30)
$$q = 1 + \frac{2n\beta A}{\lambda}(an - 1)(a\lambda + 2)e^{-\lambda a}$$

$$r = \frac{n^2\beta^2A^2}{\lambda^2}(a\lambda+2)^2 e^{-2\lambda a} - \frac{2n\beta A}{\lambda}(a\lambda+1) e^{-\lambda a}.$$

The two roots of (7.29) are

(7.31)
$$\alpha = -\frac{1 + \frac{2n\beta A}{\lambda}(an-1)(a\lambda+2)e^{-\lambda a}}{2(1-an)^2} \pm \frac{\{1 - \frac{4n\beta A}{\lambda}(1-an)[a\lambda(2an-1)+2an]e^{-\lambda a}\}^{1/2}}{2(1-an)^2}$$

Since α must be real, we require

(7.32)
$$\frac{4n\beta A}{\lambda}(1-an)[a\lambda(2an-1) + 2an]\, e^{-\lambda a} \leq 1 .$$

The sign in front of the square root in (7.31) must be chosen so that the compressibility is positive, $k_T > 0$.

By placing $A = \lambda$ in the attractive Yukawa potential, equation (7.20), and then taking the limit $\lambda \to 0$, we recover the tail potential of the Kac model [17], which is known to lead to a phase change described by the van der Waals equation:

(7.33)
$$\beta P = \frac{n}{1-an} - \beta n^2 ,$$

from which

$$\frac{\partial}{\partial n}(\beta P) = \frac{1 - 2n\beta(1-an)^2}{(1-an)^2} \tag{7.34}$$

Evaluating (7.31) in the limit $\lambda \to 0$, we find

$$\frac{\partial}{\partial n}(\beta P) = -\alpha = \frac{1 + 4n\beta(an-1) \pm \sqrt{1-8an^2\beta(1-an)}}{2(1-an)^2} \quad . \tag{7.35}$$

At very high temperature, the properties are determined by the cores. In the limit, $\beta \to 0$, (7.34) and (7.35) agree,

$$\lim_{\beta\to 0} \frac{\partial}{\partial n}(\beta P) = Q_0^2 \ . \tag{7.36}$$

For finite β, $> \beta_0$, the van der Waals description is recovered.

The above technique obviously applies to double Yukawa tails. Such potentials, ϕ, which in three dimensions have the form

$$\phi(r) = \frac{1}{r}\left(A_1 e^{-\lambda_1 r} - A_2\, e^{-\lambda_2 r}\right) , \quad 0 < r < \infty, \tag{7.37}$$

simulate intermolecular potentials quite well.

Appendix A. Evaluation of $\Gamma(x)$ from $\Gamma''(x)$.

1. Expression of $\Gamma(x)$ in Terms of a Single Constant.

From (5.36) and (5.39), for $-a < x < 2a$,

$$\Gamma''(x) = \delta''(x) - 2n^2Q_0^2\delta(x) - 2n^2Q_0^2\delta(x-a) + 2nQ_0\delta'(x-a). \tag{A.1}$$

Writing $c_0(x)$ (refer to (5.11)) as a continuous function plus a step function leads to the conclusion that $c_0''(x)$ can be expressed in terms of delta-functions,

$$c_0''(x) = 2nQ_0^2\delta(x) - nQ_0^2\delta(x-a) + Q_0\delta'(x-a) . \tag{A.2}$$

(A.2) enables (A.1) to be written

$$\Gamma''(x) = \delta''(x) - 6n^2Q_0^2\delta(x) + 2nc_0''(x) \tag{A.3}$$

or

$$(\Gamma(x) - \delta(x) - 2nc_0(x))'' = - 6n^2Q_0^2\delta(x) . \tag{A.4}$$

Since the left-hand side of (A.4) is an even function of x, there must be no odd functions appearing in the second antiderivative. Thus, a single (finite) constant, denoted by K, appears in the result

$$\Gamma(x) = \delta(x) + 2nc_0(x) - 3n^2Q_0^2|x| + K , \quad (-a < x < 2a). \tag{A.5}$$

2. Calculation of the Constant.

From (3.53) and (5.2), there follows

$$(A.6)\quad (\Gamma(x) - \delta(x)) * (\delta(x) - nc_0(x)) = n(g_0(x)-1) + nc_0(x),$$

valid for all x. In particular, at x = 0

$$(A.7)\quad (\Gamma(0) - \delta(0)) - n \int_{-a}^{a} c_0(x')(\Gamma(x') - \delta(x'))\, dx' = -n + nc_0(0)\ .$$

Using (A.5) to introduce K into (A.7) leads to the relation

$$(A.8)\quad K = \frac{n}{\beta} k_T[- n - nc_0(0) - 6n^3Q_0^2 \int_0^a x\, c_0(x)\, dx + 4n^2 \int_0^a c_0^2(x)\, dx]$$

in which the isothermal compressibility, k_T, occurs due to (2.21). In view of (5.11), all terms in (A.8) are readily calculated. The result is

$$(A.9)\quad K = a\, n^2Q_0^2\, (6 - 6an + \frac{10}{3} a^2n^2 - a^3n^3)\ ,$$

since $\frac{n}{\beta} k_T = Q_0^{-2}$ for hard cores.

Appendix B. Calculation of $\Gamma_{-2}(x-2a)$.

From (5.33), (5.36), and (5.37), the only non-zero terms in $\Gamma''(x)$ for $2a < x < 3a$ are $\Gamma''_0(x)$, $\Gamma''_{-1}(x-a)$, and $\Gamma''_{-2}(x-2a)$.

Referring to equation (A.3), we have

$$\Gamma''(x) = \delta''(x) - 6n^2Q_0^2\,\delta(x) + 2nc''_0(x) + \Gamma''_{-2}(x-2a), \qquad (2a < x < 3a). \tag{B.1}$$

The term $\Gamma''_{-2}(x-2a)$ is the additional piece, addended when $x > 2a$. From (B.1), there follows

$$\Gamma(x) = \delta(x) + 2nc_0(x) - 3n^2Q_0^2|x| + K + \iint \Gamma''_{-2}(x-2a)\,d^2x\,, \qquad (2a < x < 3a), \tag{B.2}$$

with

$$\Gamma_{-2}(x-2a) = \iint \Gamma''_{-2}(x-2a)\,d^2x\,. \tag{B.3}$$

From (5.37),

$$\Gamma''_{-2}(x-2a) = -\frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-ik(x-2a)}\,\frac{(2n^2Q_0^2+3k^2)}{(1-i\,\frac{k}{nQ_0})^2}\,dk \tag{B.4}$$

Using a partial fraction decomposition, we find

$$(B.5)\quad \Gamma''_{-2}(x-2a) = 3n^2Q_0^2\delta(x-2a) - \frac{6n^3Q_0^3}{2\pi}\int_{-\infty}^{\infty} e^{-ik(x-2a)}\,\frac{dk}{(nQ_0-ik)} + \frac{n^4Q_0^4}{2\pi}\int_{-\infty}^{\infty} e^{-ik(x-2a)}\,\frac{dk}{(nQ_0-ik)^2}\,,\quad (x > 2a).$$

The integrals are readily evaluated by contour techniques.

(B.5) can be written

$$(B.6)\quad \Gamma''_{-2}(x-2a) = 3n^2Q_0^2\delta(x-2a) - 6n^3Q_0^3\, e^{-nQ_0(x-2a)} + n^4Q_0^4(x-2a)\, e^{-nQ_0(x-2a)}\,,\qquad (x > 2a).$$

From (B.3) and (B.6), we obtain the result

$$(B.7)\quad \Gamma_{-2}(x-2a) = \frac{3}{2}\, n^2Q_0^2|x-2a| - 4n\, Q_0\, e^{-nQ_0(x-2a)} + n^2Q_0^2(x-2a)\, e^{-nQ_0(x-2a)}\,,\qquad (x > 2a).$$

Bibliography

1. T. L. Hill, Statistical Mechanics, (McGraw-Hill, New York, 1956), 189.
2. Reference 1, p. 236.
3. J. K. Percus, Phys. Rev. Letters 8, 462 (1962).
4. V. Volterra, Theory of Functionals, (Dover, New York 1959), 20.
5. J. L. Lebowitz and J. K. Percus, J. Math. Phys. 4, 116 (1963).
6. J. K. Percus, Pair Distribution Function in Classical Statistical Mechanics, in Equilibrium Theory of Classical Fluids, ed. H. L. Frisch, J. L. Lebowitz, (W. A. Benjamin, New York 1964).
7. Reference 5, p. 117.
8. See e.g. Reference 6, p. 70.
9. J. L. Lebowitz and J. K. Percus, Phys. Rev. 122, 1675 (1961).
10. J. K. Percus, Transactions of N. Y. Academy of Sciences 26, 1062 (1964).
11. L. Landau and I. Lifshitz, Statistical Physics, (Addison-Wesley, Reading 1958), 231.
12. J. K. Percus and G. J. Yevick, Phys. Rev. 110, 1 (1958).
13. M. S. Wertheim, J. Math. Phys. 5, 643 (1964).
14. J. K. Percus and S. Shanack, unpublished.
15. J. K. Percus, Many-Body Systems, CIMS Lecture Notes, Winter 1965, p. 26.

16. R. J. Baxter, Phys. Rev. 154, 170 (1967).

17. M. Kac, G. E. Uhlenbeck, and P. C. Hemmer, J. Math. Phys. 4, 216 (1963).

18. J. K. Percus and G. J. Yevick, Phys. Rev. 136, 290 (1964).

19. J. L. Lebowitz and J. K. Percus, Phys. Rev. 144, 251 (1966).

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

NYO-
1480-151 c.1

Percus

Exact solution of the first-

NYO- c.1
1480-151 Percus

AUTHOR

Exact solution of the first-
TITLE order perturbed Percus-
Yevick equation…

DATE DUE	BORROWER'S NAME

OCT 8 1970

DATE DUE